Physical Electrochemistry

Organizer: Daniel Scherson Case Western Reserve University, Cleveland, OH
Organizer: Kenneth W. Street The NASA-Glenn Research Center, Cleveland, OH
Presider: Daniel Scherson Case Western Reserve University, Cleveland, OH

Session Overview: This session is devoted to all aspects of physical electrochemistry including electrocatalytic phenomena, corrosion, semiconductor electrochemistry and other topics.

1. Multiwalled Carbon Nanotube (MWCNT) as Support for PtRu Anode Catalysts of a Direct Ethanol Fuel Cell (DEFC)

Susmita Singh and Jayati Datta, Department of Chemistry, Bengal Engg Sci University, Shibpur, Howrah, India

DEFC is one of the most promising power sources for the near future. Since the kinetics and electro-efficiency of the process strongly depend on the noble metal formulations and their dispersion on suitable support, an intensive research is devoted to decrease the catalyst loading.
This work reports an improved electro-catalytic activity for ethanol oxidation at Pt-Ru co-deposited surfaces on MWCNT support. Pt-Ru catalysts with different compositions were synthesized on pre-functionalized MWCNT by adopting sol method. The degree of surface functionalization is found to depend on the level of acid treatment. Chemical reduction of precursor salt using ethylene glycol as mild reducing agent as well as capping agent at 140^0C yields catalyst particle size of few nanometers as confirmed by XRD and TEM studies. Cyclic voltammetry, polarization study and electrochemical impedance spectroscopy were employed to evaluate the electro-catalytic phenomenon over a range of H_2SO_4 and ethanol concentrations. A spectacular negative potential shift of more than 250 mV of the onset of ethanol oxidation was observed on the Pt-Ru catalyst in comparison to Pt alone.
High mesoporous surface area of carbon nanotube can significantly increase the metal dispersion and affect particle size as well as mesoporous network of nanotubes combined with their excellent conducting properties allows a quick transport and easy accessibility of the reagent molecules to the catalytic sites enabling better performance of binary Pt-Ru system compared to Pt alone at the DEFC.

2. Thermal Energy Storage with High Energy Density and Power Density Using Macro-Encapsulated Phase Change Material

Andrey Soukhojak, David Bank, Myron Maurer and Kalyan Sehanobish, The Dow Chemical Company, Midland, MI

One approach to reduce CO_2 emissions is to use thermal energy from renewable or waste heat sources (e.g. solar radiation, heat generated by an internal combustion engine). A major challenge for this approach is the necessity to store thermal energy for at least a few hours between 1) the times when the source's available thermal power is high, but the need for heat is low and 2) the times when the need for thermal energy is high, but the source is not available. When electric energy is to be stored, electrochemical batteries and capacitors perform this task with high efficiency. However, the cost of electric energy storage is high due to expensive materials and the complexity of these devices.

Heat (thermal energy) is a primitive form of energy, but in many applications it brings utility to the user. As with electric energy storage, the primary performance measures describing thermal energy storage (TES) are energy density and power density of the device. We report on a low-cost TES prototype that challenges the energy density and exceeds the power density of lithium ion batteries. The prototype utilizes an inorganic phase change material (PCM) in combination with metallic foil macro-encapsulation to store energy as both sensible heat and latent heat in the 20-300 °C temperature range.

Working prototypes were designed which demonstrate reduction to practice for automotive and non-automotive applications. The PCM's properties and the device architecture promise benefits in a broad range of applications, including thermal management of lithium ion batteries.

3. Theoretical Aspects of Light-Activated Microelectrodes IN Redox Electrolytes

Huanfeng Zhu, Barry Miller and Daniel Scherson, Chemistry, Case Western Reserve University, Cleveland, OH

Earlier studies have shown that it is possible to generate light-activated electrodes employing a focused laser impinging at normal incidence on the surface of a semiconductor electrode immersed in an electrolyte containing a redox species. Implementation of this novel concept using n-InP disk in solutions of ferrocene in well-supported acetonitrile electrolytes at high positive potentials, φ_{bias}, yielded a behavior closely resembling that of conventional metallic microelectrodes. This contribution will explore theoretically the behavior of such semiconductor-based, light-activated microelectrodes in redox electrolytes utilizing a commercial software to solve self-consistently the transport equations for solid state and solution phase species and the electrostatic potential within the semiconductor phase subject to the appropriate boundary conditions under steady state. The light-limited currents for such spatially-localized microelectrodes observed for high voltage bias, φ_{bias}, under normal irradiation and strict axisymmetric geometry were found to be proportional to the photon flux intensity. In addition, the results of these simulations afforded strong evidence that under high φ_{bias}, holes generated by the light on an n-type semiconductor escape beyond the edge of the illuminated disk, leading to a net increase in the predicted current and thus in the effective area of the light activated microelectrode. For the parameters selected for this simulation, the fraction of the total current flowing through the illuminated area of n-InP amounts to 42%. In contrast, for n-Si, an indirect band semiconductor, under the same conditions, this fraction is reduced to 27% as would be expected since the holes are generated deeper into the material.

4. Funtional Neural Stimulation: Oxygen Reduction On Supported Iridium Oxide in Neutral Media

Youjiang Chen, **Michelle A. Rasmussen** and Daniel Scherson, Chemistry, Case Western Reserve University, Cleveland, OH

Iridium oxide, IrO_x, ranks among the most promising electrode materials for functional neural stimulation applications. In particular, IrO_x is fully biocompatible and exhibits supercapacitive behavior, i.e. it can store reversibly large amounts of charge, which can be injected or released over very shorts period of time. Yet another attribute of this material, which has not yet been thoroughly studied, relates to its very large overpotential for dioxygen reduction. This is of special importance, as certain products of O_2 reduction, e.g. superoxide and peroxide, are known to chemically attack the nerve walls impairing signal transmission. This study examines O_2 reduction on IrO_x supported on various substrates in phosphate buffer aqueous solutions (pH = 7). As will be shown, the potential region where IrO_x exhibits pseudocapacitive properties is largely positive to the onset of O_2 reduction; hence, a significant fraction of the charge stored in the film becomes available for the negative charge injection involved in neural stimulation without generation of hazardous species.

5. On the Physical Meaning of Constant Phase Element

Bernard Tribollet[1], Mark E. Orazem[2], Isabelle Frateru[3] and Vincent Vivier[1], (1)Laboratoire des Interfaces et Systèmes Electrochimiques,, Université Pierre et Marie Curie, Paris cedex 05, France, (2)Department of Chemical Engineering, University of Florida, Gainesville, FL, (3)Laboratoire de Physico-Chimie des Surfaces, ENSCP, Paris, France

Constant phase elements (CPE) are used extensively in electrical equivalent circuits used to analyze experimental impedance data. While CPE behavior is observed experimentally, its interpretation has been controversial for many years. However, if the CPE behavior can be considered to be evidence of frequency dispersion, its origin can be due to dispersion of the resistance, of capacitance, or both. Recent work has shown that Local Electrochemical Impedance Spectroscopy (LEIS) can be used in some cases to assess the influence of local variations on the CPE behavior seen in global measurements, and a distinction between 2D and 3D distributions could be observed. Two different formulas are proposed to relate the CPE parameters to the mean capacitance for 2D and 3D distributions. Different origins of the frequency dispersions are analyzed: geometrical effect inducing a primary current distribution, a variation of oxide layer thickness, a variation of the oxide layer resistivity according to the normal coordinate. The particular case of a CPE with an exponent of 0.5 has a particular meaning because it could be related only to a diffusion process or to a porous electrode as described by de Levie. In all cases, the high-frequency global impedance response has the appearance of a constant phase element (CPE) but can be considered to be only an apparent CPE because the CPE exponent is a function of frequency.

6. Optical Interfacial Microcalorimetry

Bin Hai and Daniel Scherson, Department of Chemistry, Case Western Reserve University, Cleveland, OH

A method in herein described that allows for the enthalpy of an interfacial process to be determined in situ. It is based on probe beam deflection measurements performed through the back of an optically transparent solid media which support a very thin film of a metal electrode in contact with the electrolyte solution using a laser beam propagating parallel to the interface. Experiments were performed using a Au electrode in sulfuric acid aqueous solutions. The results obtained based on numerical simulations were found to be consistent with an enthalpy for the reduction of a monolayer of Au oxide on the order of 90 kcal/mol (heat being released from the interface). Rather unexpectedly, a positive enthalpy of about the same magnitude was also found for the formation of the Au oxide layer.

7. Impedance of a Microelectrode in SECM Experiments

Vincent Vivier, Michel Keddam, Nicolas Portail and Dao Trinh, Laboratoire Interfaces et Systèmes Electrochimiques,, Université Pierre et Marie Curie, Paris cedex 05, France

Scanning electrochemical microscopy (SECM) has received a significant attention these last decades using microelectrodes (UME) as local probes. Due to their small dimension, in the range of micrometer or less, mass transport is controlled totally by hemispherical diffusion between the solution bulk and the electrode surface. The steady-state current flowing through the UME is thus limited to a value I_{inf} that is reached in a very short time, and is proportional to the electrode radius a.

The present work is intended to describe the experimental results obtained in both positive and negative feedback modes when impedance measurement is performed at the UME.

When the substrate is an insulator (negative feedback mode), the radial contribution of diffusion at the microelectrode is evidenced in the low frequency range. Its contribution depends on the distance between the UME and the insulating substrate, and also on the total UME dimension.

When the substrate is a conductor (positive feedback mode), the diffusion impedance is comparable to that obtained with a rotating disk electrode.

It will also be shown that experimental results were in good agreement with numerical calculations performed by FEM.

8. Ohmic Microscopy

Youjiang Chen, Huanfeng Zhu and Daniel Scherson, Department of Chemistry, Case Western Reserve University, Cleveland, OH

The passage of current through an electrolyte brings about changes in the electrostatic potential, φ_{sol}, within that phase, which allows spatially-resolved capacitive currents at electrode|electrolyte interfaces to be recorded *in situ* by monitoring the ohmic drop in the electrolyte, $\Delta\varphi_{sol}$, using two microreference electrodes. Measurements were performed in 0.1 M H_2SO_4 aqueous solutions using Au and Pt either as single, or dual working electrodes, i.e. connected to one another. Plots of $\Delta\varphi_{sol}$ vs E, the potential of the dual Au|Pt electrode with respect to the main reference electrode, recorded during voltammetric cycles, yielded curves bearing features characteristic of the Au|0.1 M H_2SO_4 or Pt|0.1 M H_2SO_4 interface depending on whether the microreference electrodes were placed close to the Au or Pt electrode surface, respectively. Also to be presented are the results of mathematical simulations based on the solution of Laplace's equation, including the effect of the actual size of the probe.

Women in Electrochemistry (1)

Organizer: Heidi B. Martin Case Western Reserve University, Cleveland, OH
Organizer: Irina Serebrennikova Energizer, Westlake, OH
Organizer: Carol Korzeniewski Texas Tech University, Lubbock, TX
Presider: Heidi B. Martin Case Western Reserve University, Cleveland, OH

Session Overview: The Women in Electrochemistry Symposium will highlight research from women in the field of electrochemistry from all across the globe, demonstrating the broad impact women are making in the field. Additional programming beyond the technical symposium will provide opportunities for networking among faculty and students and include formal discussion of issues in recruiting and retaining women in all fields of science and engineering.

9. Making the Most of An Electrochemically Critical Material: Self-Wiring Metallic Nanoskins of Ruthenium Dioxide Onto (dirt-cheap) Glass Filter Paper

Debra R. Rolison, Christopher N. Chervin, Jeffrey W. Long, Alia M. Lubers and Katherine A. Pettigrew, Code 6170, Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, DC

Deposition of RuO_2 onto porous SiO_2 substrates via subambient decomposition of ruthenium tetroxide from nonaqueous solution leads to a self-wired formation of nanowebs and ultimately nanoscale films of RuO_2. The physical properties of the resultant nanoscale ruthenia differ significantly depending on the nature of the porous silica. In aerogels modified at RuO_2 weight loadings of ~40 wt%, the metallic nanoweb displays conductivity on the order of 0.5 mS/cm [1], whereas the RuO_2-modified glass membranes, having a weight loading of 5 wt%, display metallic conductivity on the order of 0.5 S/cm. Although the RuO_2 phase is constrained to a nanoscale skin, the $RuO_2||SiO_2$ fiber membranes are electrically addressable, capable of supporting fast electron-transfer reactions, express an electrochemical surface area of ~90 m^2g^{-1} RuO_2, and exhibit energy storage in which 90% of the total electron–proton charge is stored at the outer surface of the ruthenia phase. The electrochemical capacitive response indicates that the nanocrystalline RuO_2 shell can be considered to be equivalent to an exfoliated oxide layer stabilized by the supporting silica fiber. [1] J.V. Ryan, A.D. Berry, M.L. Anderson, J.W. Long, R.M. Stroud, V.M. Cepak, V.M. Browning, C.I. Merzbacher, and D.R. Rolison, *Nature* **2000**, *406*, 169.

10. Electrodeposited Silica Films: How to Grow Your Own Chia Pet

Maryanne M. Collinson and Dong Dong, Chemistry, Virginia Commonwealth University, Richmond, VA

Silica films can be formed on conducting surfaces by electrogenerating hydroxide ions via the reduction of water/oxygen in the presence of an alkoxysilane. The electrogenerated hydroxide ions serve as a catalyst and cause the silica sol to gel at the electrode surface (but not in the bulk of the solution), thus forming a silicate film. In this presentation, cathodic electrodeposition as a means to prepare porous silica films in a recessed electrode will be described.

11. Alloys and Oxides in the Electrochemical Oxidation of Alcohols On Pt-Based Bimetallic Catalysts

Denis R. M. Godoi, Joelma Perez and **H. Mercedes Villullas**, Departamento de Físico Química, Instituto de Química - Universidade Estadual Paulista (UNESP), Araraquara (SP), Brazil

Pt-Ru/C and Pt-Sn/C catalysts were prepared in water/n-heptane/AOT microemulsions and heat treated in different atmospheres to modify the amounts of their alloyed and oxide phases. Because particle growth was avoided using mild temperature conditions, the studies reported here were conducted in the absence of particle size effects. Structure and particle size were characterized by X-ray diffraction and transmission electron microscopy. All catalysts showed particle sizes around 3 nm, narrow particle size distributions (polydispersion ≤20%) and uniform distribution on the carbon support. Studies of differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), and `in situ` dispersive X-ray absorption spectroscopy (DXAS) were also done. Oxidation of adsorbed CO was used to probe surface conditions. The catalytic activities of Pt-Ru/C materials for the electrooxidation of methanol and of Pt-Sn/C catalysts for ethanol oxidation were studied by potential sweeps and chronoamperometry in sulfuric acid solutions.
Variations in the amount of alloyed and oxide phases produce changes in the Pt d band occupancy which, in turn, affects the electrocatalysis of alcohol oxidation and adsorbed CO removal. The results show that oxides and alloys play different roles in those processes. Analysis of the relative contributions of electronic effects and the bifunctional mechanism in the electrocatalysis of methanol, ethanol and CO oxidations indicates that the generally accepted correlation between the ability to oxidize adsorbed CO and the enhancement of alcohol electroooxidation needs revision.

Acknowledgments. To FAPESP, CNPq and FINEP for financial support, and to the Brazilian Synchrotron Light National Laboratory (LNLS) for assisting the DXAS measurements.

12. Poly(Vinyl Ferrocene) Redox Behavior in Ionic Liquids and Their Applications

Yijun Tang[1], **Xiangqun Zeng**[1] and Gary A. Baker[2], (1)Department of Chemistry, Oakland University, Rochester, MI, (2)Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN

Poly(Vinyl Ferrocene) Redox Behavior in Ionic Liquids and Their Applications Xiangqun Zeng1, Yijun Tang1, Gary Baker2 1Department of Chemistry, Oakland University, Rochester, MI 48309, USA 2Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA Interactions between poly(vinyl ferrocene) (PVF) and ionic liquids (ILs) were studied with electrochemical methods. The study provided an insight on how ILs dope into and undope from the PVF matrix. A square model was proposed to describe the above processes. The PVF can be electrochemically switched between its reduced state (R) and its oxidized state (O) in the square model. In addition, upon PVF-IL contacting, PVF transits gradually from an electrochemically inactive status (Ri or Oi) to a fully activated status (Rf or Of). Therefore, two independent processes are identified in the PVF-IL interaction: a faradic process and a non-faradic process. The faradic process involves electron transfer at the electrode/polymer interface, where R is oxidized to O or O is reduced to R. The non-faradic process involves no electron transfer, where the PVF (R or O) is getting electrochemically activated. The complicated and strong polymer/IL interaction can be used in the applications such as accelerated polymer relaxation, polymer modification, and structure tuning. We studied how to adjust PVF structure by ILs so that PVF was capable of doping/undoping GGG peptide. The effect of tuning is determined mainly by the anions of the IL. The rod-shaped anions are similar to the shape of GGG peptide and are more efficient in tuning PVF for GGG doping and releasing.

Computational Chemistry (1)

Organizer: Peter Politzer University of New Orleans, New Orleans, LA
Organizer: Jane S. Murray University of New Orleans, New Orleans, LA
Presider: Peter Politzer University of New Orleans, New Orleans, LA
Presider: Jane S. Murray University of New Orleans, New Orleans, LA

Session Overview: During the past 20 years, remarkable advances in both methodology and processor technology have allowed computational chemistry to evolve into an important tool for addressing problems of practical interest and significance. The presentations in this symposium are intended to illustrate a wide range of applications, including fuel cells, nanomaterials, molecular electronics, sensors, nonlinear optical activity, signal transduction, enzyme activities, actinide chemistry and anti-cancer agents. There will also be discussion of different aspects of intermolecular complexes (including the very active area of halogen bonding), metal/DNA interactions, and new concepts in analyzing chemical reactions and in modeling complex systems. Acknowledgements: We greatly appreciate the support provided by the U. S. Office of Naval Research and the Computers in Chemistry Division of the American Chemical Society.

13. Current-Voltage Characteristics through Molecular Junctions by Ab Initio Techniques

Jorge M. Seminario, Departments of Chemical Engineering, Electrical Engineering, and Materials Science and Engineering, Texas A&M University, College Station, TX

We analyze the behaviour of several types of molecules of interest for chemical and biological sensing attached to two-terminal junctions in order to explain their electrical characteristics based on molecular orbital theory using ab initio density functional methods. We find for instance that the application of a direct bias potential with respect to the molecular dipole smoothen down the potential of the junction because the approach of the highest occupied molecular orbital (HOMO) energy to the lowest unoccupied molecular orbital (LUMO) when the direct bias voltage is increased. However, a reverse bias increases the HOMO-LUMO gap energy and constrains the molecular potentials to stronger changes in a shorter region inside the junction as the bias potential increases. The analysis is predictive when using largely validated methods (for molecular potentials). Non-yet-validated (against experiments) procedures (for molecular currents) are also fully compatible with the results of the validated methods. The geometry of the selected extended molecules are optimized then followed by self-consistent calculations that include electric fields (dipole) that yield, between the gold ends, voltages for which the current through the molecule is calculated using our procedure GENIP for electron transport.

14. Modeling CO2 Capture by Molecular Organic Frameworks

Janice A. Steckel, U.S. Departement of Energy, National Energy Technology Laboratory, Pittsburgh, PA

Molecular organic frameworks (MOF), nanoporous materials consisting of metal or metal oxide vertices interconnected by organic linker molecules, present a number of properties of interest for possible CO_2 sorption or separation processes. In this project, computational methods are used to study the interaction of CO_2 with several interesting MOF materials. The polymeric material $[Ni(bipy)(DBM)_2]_n$ (bipy = 4,4′-bipyridyl, DBM = dibenzoylmethanate) forms a flexible ladder-and-platform structure. CO_2 uptake by this material is initially weak until a threshold pressure is reached, after which uptake is strong. ATR-IR experiments have produced evidence that a structure change may accompany the dramatic change in CO_2 sorption. Computational methods are used to identify the nature of the interaction of CO_2 with the material and the structural changes that accompany CO_2 sorption. CO_2 adsorption in the rigid MOF $Cu_2(Bz)_4$-Pyz is also investigated. In contrast to the flexible Ni-based material, this material is more rigid and it is shown that CO_2-CO_2 interactions are important.

15. Challenges In the Design of Active and Durable Fuel Cell Catalysts

Perla B. Balbuena, Department of Chemical Engineering, Texas A&M University, College Station, TX

Metal nanoparticles used as catalysts in low-temperature fuel cells are expected to provide the necessary activity and stability such that the fuel cell performance is minimally affected by catalytic decay. In particular, the slow kinetics of the oxygen reduction cathode reaction and the cost and scarcity of platinum -so far the best catalyst for this reaction- has motivated a very intense multidisciplinary field of research especially oriented to finding the best alloy nanomaterials.
In this talk I will discuss some of the most important challenges associated with the design of efficient alloy nanocatalysts, due to the harsh chemical environment where these catalysts work. Specifically, characterization of surface composition is crucial to understand reaction mechanisms. Systematic studies will be presented addressing thermodynamics and kinetic aspects of surface segregation phenomena in alloy nanoparticles. Further, how surface segregation trends may change under the presence of adsorbates and under dynamic reaction conditions will be discussed in the context of rational design of nanocatalysts. In acid medium, corrosion reactions also play a significant role. We have recently hypothesized that metal corrosion starts with the formation of a surface oxide and we have shown through a systematic analysis the role of certain alloy elements on the stabilization of surface platinum atoms. Application of new techniques for the investigation of such stabilizing effect on alloy surfaces will be discussed.

Energy Storage and Energy Conversion: Electrocatalysis (1)

Sponsor: CH Instruments; Cincinnati Student Chapter, ECS
Organizer: Shouzhong Zou Miami University, Oxford, OH
Organizer: Yuriy Tolmachev, Dr. Kent State University, Kent, OH
Presider: Yuriy Tolmachev, Dr. Kent State University, Kent, OH

Session Overview: Fuel cells are efficient energy conversion devices. In order to make fuel cell technology viable in daily life, several technical challenges need to be overcome. In this sub-symposium, a subset of these challenges will be discussed. Topics to be covered include, but are not limited to: durability of fuel cells, Pt loading reduction of fuel cell catalysts, new catalysts, and applications of spectroscopic methods to fuel cell problems.

16. Broad-Band Sum Frequency Generation to Study Electrochemical Interfaces

Rachel L. Behrens, Alexei Lagutchev, Dana D. Dlott and Andrzej Wieckowski, Department of Chemistry, University of Illinois, Urbana, IL

Broad-band sum frequency generation spectroscopy (BB-SFG) is a novel method to perform chemical analyses of electrode surfaces to examine details of surface electrochemical reactions which are not fully understood. SFG is based on a second order nonlinear optical process that is forbidden in centrosymmetric media. Therefore, SFG is intrinsically interface-sensitive and enables surface chemical measurements without contribution from the bulk. With the aid of a femtosecond IR laser, we probe vibrational transitions of adsorbates in real time on the electrode surface as the potential at the surface is scanned at rates up to 5 mV/s.

With the recently renewed interest with formic acid as a viable fuel for fuel cells, we have used this technique to study the intermediates of the oxidation of formic acid to CO on platinum electrodes. As CO continues to be the cause for a decrease in efficiency and activity for platinum electrodes and is the leading intermediate in the most common oxidation reactions. Therefore, we have studied this CO species generated from both formic acid and CO-saturated media to observe site conversion of the CO species on the Pt surface with respect to concentration, composition of electrolyte and potential. Studies of other reaction intermediates and adsorbates will also be addressed. These factors will demonstrate the sensitivity of the BB-SFG technique to the adsorbed species, and its capability to follow site conversions of the species on the electrode surface.

17. In Situ Structural Characterisation of PEM Fuel Cell Nanoparticle Catalysts

Andrea E. Russell, Prof.[1], Peter P. Wells[1], Beatrice Tessier, Miss.[2], Sarah L. Hudson[2], Sarah Ball[2] and David Thompsett[2], (1)School of Chemistry, University of Southampton, Southampton, United Kingdom, (2)Johnson Matthey Technology Centre, Reading, United Kingdom

The state of nanoparticles under electrochemical conditions such as those in either wet electrochemical or PEM fuel cell environments may not necessarily be correctly represented by ex situ characterisation methods such as TEM, powder XRD, or XPS. A full understanding of the structure of such materials can only be obtained if the characterisation is completed in the working environment. A Taking Pt/C and Pt_3Co/C cathode catalysts as examples we will show the importance of the environment in structural characterisation using both extended X-ray absorption fine structure (EXAFS) and XRD measurements. Data will be presented for in situ characterisation in a wet electrochemical cell and operando using a miniature PEM fuel cell.

18. Pt Single Crystal Electrodes as Standards in the Study of Reactions Over Nanoparticle Catalyst

Carol Korzeniewski and Prachak Inkaew, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX

Single crystal electrodes are being used as standards to determine the cleanliness and baseline response of the electrochemical system prior to measurements on nanoscale catalyst materials. This presentation will discuss results for Pt(111), Pt(100) and Pt(335) (Pt(s)-[4(111) x (100)]) electrodes in sulfuric acid solutions and focus on the oxidation kinetics of adsorbed CO measured in potential step experiments. It has been known for some time that the electrochemical oxidation of a CO monolayer at full coverage on Pt(111) and stepped surfaces with the Pt(s)-[n(111) x (111)] structure occurs in accord with a simple model based on the Langmuir-Hinshelwood (LH) mechanism. We are examining CO oxidation under conditions that lead to apparent deviations from the simple LH model. One condition studied is the oxidation of CO from a monolayer initially at sub-saturation coverage. In potential step experiments, the shape of current-time transients is strongly influenced by the initial CO coverage. It will be shown that the LH model can predict these current-time responses when the set of reaction rate equations is solved numerically and account is taken of the initial sub-saturation coverage of CO on the electrode. A second condition examined is the oxidation of CO at saturation coverage on nanostructured Pt electrodes. The oxidation of a CO monolayer initially at saturation coverage gives current-time transients that are more complex than predicted by the LH model. The responses are examined by solving mean field equations that allow for multiple types of reaction sites on the nanostructured surfaces.

19. Fine Tuning of Electrochemical Activity

Dennis van der Vliet[1], Chao Wang[1], Dusan Strmcnik[1], Christopher Lucas[2], Nenad Markovic[1] and **Vojislav Stamenkovic**[1], (1)Argonne National Laboratory, Argonne, IL, (2)University of Liverpool

Tuning of the electronic and structural properties of nanocatalysts can potentially lead towards the superior catalytic enhancements that have been reported recently for the Pt-skin surfaces.
We have proposed that surface modifications induced by the additional elements, and consequent catalytic enhancements could occur through the following effects: (1) Electronic effect, due to changes in the metallic d-band center position vs. Fermi level; and (2) Structural effect, which reflects relationship between atomic geometry, and/or surface chemistry, i.e., dissolution – surface roughening.
The similar levels of catalytic enhancement have been established for corresponding nanoscale materials. In addition to electronic properties we have found how catalytic activity could be affected by the arrangement of surface defects on nanoscale surfaces. Ability to control surface and near

surface catalyst properties enables fine tuning of catalytic activity and stability of nanoscale surfaces.

20. Size and Shape Controlled Pt-M Alloy Nanoparticles for Fuel Cells

Shouzhong Zou, Hongzhou Yang and Lin Dai, Department of Chemistry & Biochemistry, Miami University, Oxford, OH

Increasing the kinetics of oxygen reduction and small organic oxidation on Pt catalysts is a key challenge in fuel cell development. An effective way to tackle this problem is to use Pt-based alloy nanoparticles. In this presentation, electrocatalytic activity studies of various Pt-M alloy nanoparticles with size and shape controlled will be discussed. These particles, including PtNi, PtCo and PtCu, were synthesized by wet-chemical approaches with organic solvents at elevated temperatures. Their size and shape were controlled by various surfactants. Results from structural characterization will be shown. The electrocatalytic activity studies reveal that the PtNi particles are very active for oxygen reduction, exhibiting more than 20 fold specific activity and mass activity improvement as compared with the commercial Pt/C catalysts. The PtCo and PtCu particles exhibit enhanced methanol oxidation activity as compared to Pt/C catalysis. In addition, PtCu particles also exhibit significant increase in formic acid oxidation kinetics. Possible mechanisms of the activity improvement will be discussed in the presentation.

Forensic Science (1)

Sponsor: Thermo Scientific
Organizer: Douglas Rohde Lake County Crime Laboratory, Painesville, OH
Organizer: John Goodpaster Indiana University Purdue University Indianapolis (IUPUI), Indianapolis, IN
Organizer: Frank Miller Cuyahoga County Coroner's Office, Cleveland, OH
Presider: John Goodpaster Indiana University Purdue University Indianapolis (IUPUI), Indianapolis, IN

Session Overview: The Forensic Science Symposium will offer participants an overview of prevalent chemical principles, methods, instrumentation and research involved in the analysis of physical evidence and their application to the legal system.

21. Applications of Multi-Variate Statistics to Forensic Science

John Goodpaster, Department of Chemistry and Chemical Biology, IUPUI, Indianapolis, IN

Upon being presented with a questioned and known sample of evidence, the duty of the forensic scientist is to evaluate if the two samples may share a common origin. This can be accomplished by examining class characteristics, or features that can distinguish groups of samples from one another but cannot individualize an item. Hopefully, the probability of two unrelated samples having indistinguishable class characteristics is low. However, the burden is on the forensic scientist to evaluate this risk by demonstrating that the sample type in question is inherently diverse. Furthermore, reliable laboratory techniques must exist that can discern this diversity in both pristine and evidentiary samples.

Chemometric techniques have been increasingly used to study data and sample types that are relevant to forensic science. This talk will discuss the use of multi-variate statistical methods such as agglomerative hierarchical cluster analysis, principal components analysis and discriminant analysis on various types of data such as chromatograms, mass spectra, UV-visible absorbance spectra and FTIR spectra. Applications of chemometrics to forensic samples in our research has included the analysis of human hair, cotton fibers and automotive clearcoats by UV-visible microspectrophotometry, pigmented inks by pyrolysis gas chromatography-mass spectrometry (GC-MS), black electrical tape by FTIR and ignitable liquids by GC-MS. By combining instrumental and statistical techniques, issues such as the extent to which evidence can be truly differentiated, which analytical techniques are more discriminating, and quantitative associations of questioned and known samples can be addressed.

22. The Lethal Potential of the American IED: Velocity, Momentum and Kinetic Energy Measurements of Pipe Bomb Container Fragments

Joshua Cummins, Neoshia Roemer and John Goodpaster, Department of Chemistry and Chemical Biology, IUPUI, Indianapolis, IN

The most common improvised explosive device (IED) in the United States is the pipe bomb, however, there is little information available concerning the morphology or the lethality of pipe bomb container fragments. The primary construction materials for these devices are PVC, black steel, or galvanized steel pipe and the most common explosive fillers are black powder, black powder substitutes or smokeless powder. In this experiment, eleven IEDs composed of various materials were ignited via an electric match through a drilled end cap. The explosions were recorded via high speed filmography with frame rates up to 30,000 frames per second. This data was then analyzed for velocity estimates in two dimensions. Post -blast debris was analyzed simultaneously in order to identify filmed fragments and to compare fragment characteristics with their respective filler. The maximum velocity estimate for all devices was 1207 meters per second. It was also found that the number of fragments and their velocities increased with the power of their respective fillers. Devices containing black powder substitutes such as Pyrodex or Triple Seven exhibited less fragmentation and their fragments achieved lower velocities compared to devices containing double-base smokeless powder. Fragments collected from the double-base smokeless powder devices exhibited a jagged edge profile, known as stepping, typically seen in high explosive fragmentation. This trend was not observed the edge profiles of Triple Seven and Pyrodex device fragments.

23. Evaluation of the Odor Compounds Sensed by Explosive-Detecting Canines

Erica Lotspeich, Joshua Cummins and John Goodpaster, Department of Chemistry and Chemical Biology, IUPUI, Indianapolis, IN

Although canines are regularly used to detect explosives, the means by which they accomplish this task is not well understood. In particular, the factors that govern the amount of explosive vapor that is available to a canine are often confused. For example, it is a common misconception that the amount of explosive itself is the chief contributor to the amount of available odor. In fact, the concept of odor availability is decidedly more complex. Odor availability depends not only on the amount of explosive material, but also the explosive vapor pressure, the rate with which the explosive vapor is transported from its source, the extent to which the explosive degrades into more (or less) volatile substances and the degree to which the explosive is confined. Measurements using headspace gas chromatography demonstrate that for a pure liquid explosive such as nitromethane, the concentration of explosive vapor is independent of the amount of explosive present in the headspace vial. Also, the flux of nitromethane vapor from sealed containers with perforated lids depends upon the hole diameter, not sample amount. For explosives that are not intrinsically volatile, however, the composition of their vapor may not include the explosive itself. Hence, headspace solid phase microextraction (SPME) has been used to determine what compounds are present – particularly those that are directly related to the explosive (and not its surrounding matrix). Several single- and double-base smokeless powders have been analyzed in this way and energetic compounds such as nitroglycerin and dinitrotoluene have been identified.

24. Association of Evaporated Ignitable Liquids Using Gas Chromatography-Mass Spectrometry and Chemometric Procedures

John W. McIlroy, BS[1], Jamie M. Baerncopf, BS[2], Ruth Waddell Smith, Ph.D.[1], A. Daniel Jones, Ph.D.[3] and Victoria L. McGuffin, Ph.D.[4], (1)Department of Chemistry, Michigan State University, Forensic Science Program, School of Criminal Justice, Michigan State University, East Lansing, MI, (2)Forensic Science Program, School of Criminal Justice, Michigan State University, East Lansing, MI, (3)Department of Chemistry, Michigan State University, Department of Biochemistry, Michigan State University, East Lansing, MI, (4)Department of Chemistry, Michigan State University, East Lansing, MI

Chemometric procedures are becoming increasingly useful for the evaluation of petroleum fuels and other ignitable liquids in arson investigations as well as environmental spills. Through such procedures, it is generally possible to identify the type of fuel and, in some cases, to associate it with the neat liquid. However, the identification of the source becomes more difficult if the sample has been evaporated or weathered. Six different ignitable liquids (diesel, gasoline, torch fuel, paint thinner, adhesive remover, and lamp oil) were analyzed by gas chromatography-mass spectrometry (GC-MS). Each sample was then evaporated to different degrees (10%, 25%, 50%, and 75%) and then re-analyzed by GC-MS. Pearson product moment correlation (PPMC) coefficients and principal components analysis (PCA) were used to associate the evaporated liquid back to the neat liquid. Prior to chemometric analysis, data pretreatment was performed in order to minimize non-chemical variance between the samples. The pretreatment procedures included smoothing, retention time alignment, normalization, and scaling of the total ion chromatogram. Two different smoothing techniques were used, a fast Fourier transform smoothing function as well as a Savitzky–Golay smoothing function. A correlation optimized warping algorithm and a peak matching algorithm were investigated for retention time alignment. Normalization by peak area and by peak maximum was also investigated. The effect of scaling using mean-centering and autoscaling was also studied. The effect of each of these data pretreatment procedures on the association of the evaporated liquid to the corresponding neat liquid was evaluated based on PPMC and PCA results.

25. Evaluation of Aqueous Salt Solutions as Refractive Index Immersion Liquids in the Analysis of Forensic Evidence

Katiana Whitaker and Gina Ammerman, MS, Chemistry, IUPUI, Indianapolis, IN

Trace evidence analysis is a major component of forensic science. Trace materials are examined using a variety of microscopes. Examinations include morphology, chemical and physical characteristics, size, unique markings and chemical identification. One of the more common microscopic techniques is the determination of refractive index of small particles. Ultraviolet absorption microspectrophotometry is also commonly used on trace evidence. It is important to be able to mount a particle on a slide using a refractive index liquid that does not absorb in the ultraviolet region so that both refractive index and UV absorption can be measured at the same time on the same particle. Commonly used mounting media absorb in the ultraviolet region, therefore, a mounting media needs to be used with no ultraviolet absorption. At present, the most commonly used refractive index liquids absorb broadly in the ultraviolet region of the spectrum above 200 cm-1During this study, multiple concentrations of sodium chloride solutions are measured for the absorption in the ultraviolet region using a CRAIC microspectrophotometer. The refractive index values of these concentrations are also measured using a refractometer. Results showed no UV absorbance over the range of concentrations studied. Aging studies carried out on the salt solutions showed no UV absorptions but did show changes in refractive index with time. Further analysis will be done to determine and mitigate the factors causing the increasing refractive index. Light degradation and refractometer stability will also be examined.

Functional Materials: Biofunctional Materials (1)

Organizer: Horst Von Recum Case Western Reserve University, Cleveland, OH
Organizer: Joerg Lahan University of Michigan, Ann Arbor, MI

Session Overview: This sesssion will cover all manner of materials either based on biological design, modified with biomolecules and/or used in biomedical applications. Applications include self-assembling materials, tissue engineering, and drug delivery.

26. Scaffolds Based On Degradable Alginate Hydrogels and Poly(lactide-co-glycolide) (PLGA) Microspheres for Stem Cell Culture

Randolph Ashton[1], **Akhilesh Banerjee**[2], Supriya Punyani[3], David Schaffer[1] and Ravi S. Kane[2], (1)Department of Chemical Engineering, University of California Berkeley, Berkeley, CA, (2)Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY, (3)Procter and Gamble, Bangalore, ID, India

We describe a method for creating alginate hydrogels with adjustable degradation rates that can be used as scaffolds for stem cells. Alginate hydrogels have been widely used for cell culture and in tissue regeneration applications; however, alginate hydrogel implants can take months to disappear from sites of implantation. By incorporating poly(lactide-co-glycolide) (PLGA) microspheres loaded with alginate lyase into alginate hydrogels, we demonstrate that alginate hydrogels can be enzymatically degraded in a controlled and tunable fashion. We demonstrate that neural progenitor cells (NPCs) can be cultured and expanded in vitro in this degradable alginate hydrogel system. Moreover, the expansion rate of NPCs can be controlled by tuning the rate of degradation. In ongoing work, we are also investigating how the stiffness of these hydrogels influences the differentiation of NPCs. Degradable alginate hydrogels encapsulating stem cells may thus be widely applied to develop novel therapies for tissue regeneration.

27. Novel Nitric Oxide Releasing Poly(diol citrate) Elastomers for Soft Tissue Engineering

M. Concepcion Serrano[1], Haichao Zhang[2], Michele Jen[1], Melina Kibbe[3] and Guillermo A. Ameer[1], (1)Biomedical Engineering Department, Northwestern University, Evanston, IL, (2)University of Washington, (3)Department of Surgery, Northwestern University Feinberg School of Medicine, Division of Vascular Surgery, Chicago, IL

Neointimal hyperplasia and thrombogenicity continue to be significant problems for the long-term function of vascular grafts. A promising strategy to address these problems is the use of nitric oxide, which has been shown to have positive effects on both processes. Nitric oxide (NO) is a small signalling molecule with critical roles in the cardiovascular homeostasis. In our group, we have developed novel NO-releasing poly(diol citrates) able to provide a localized and sustained NO release. The prepolymers are synthesized by a polycondensation reaction of citric acid, aliphatic diols and N,'N-bis(2-hydroxyethyl)-ethylendiamine, with subsequent post-polymerization for crosslinking. The resulting polymers are elastomers and can be easily processed into a desired shape. Diazeniumdiolation of the secondary amine groups within the polymer network leads to NO release, which can be customized by varying the diol chain length or the molar ratio of amine groups. In vitro studies with endothelial and smooth muscle cells have demonstrated adequate biocompatibility of these polymers. Successful coating of polytetrafluoroethylene (PTFE) grafts has been achieved, with significant NO release at 37ºC for more than 3 days. Although preliminary, these encouraging results justify further investigation into the use of these NO-releasing elastomers.

28. Electrospun Poly (2-hydroxyethyl methacrylate) as Low-Fouling Scaffolds

Bo Zhang, Reza Lalani and Lingyun Liu, Chemical and Biomolecular Engineering, University of Akron, Akron, OH

To prepare low-fouling and biocompatible polymers for biomedical applications in nano-scale, the electrospinning approach was applied to fabricate poly (2-hydroxyethyl methacrylate) (pHEMA) nanofibers. In this study, pHEMA was prepared by free radical polymerization, initiated with ammonium persulfate and sodium persulfate, and subsequently electrospun to generate fibrous scaffolds. The structure and morphology of electrospun fibrous scaffolds were investigated by scanning electron microscopy (SEM). Confirmed by SEM images, the average diameters and porosities of the electrospun fibers can be well controlled by adjusting electrospinning parameters, including solution concentration, syringe flow rate, voltage, and needle tip-collector distance. Fiber diameters ranging from 150nm to 1.5μm were realized. Meanwhile, Enzyme-Linked ImmunoSorbent Assay (ELISA) was applied to determine human plasma fibrinogen adsorption on electrospun pHEMA fibers. It is demonstrated that the electrospun pHEMA nanofibers are highly resistant to protein adsorption and can serve as desirable scaffold materials for tissue engineering applications where low biofouling is required.

29. Elastic Surfaces for Cell Detachment Using a pNIPAAm Copolymer

Elaine L. Lee and Horst A. von Recum, Department of Biomedical Engineering, Case Western Reserve University, Cleveland, OH

Cells implanted following injury may remodel undesirably with improper mechanical stimulation from surrounding tissue. Proper cell conditioning in vitro before implantation can lead to extracellular matrix (ECM) growth that more closely mimics native tissue, and scaffolds are often used to promote ECM growth. However, because of adverse effects (eg, cytotoxicity, inflammation) from polymer degradation, implanting intact tissue without a scaffold is also highly desirable. Previous groups have created devices that stretch cells but require damaging treatment for removal, or conversely, devices that allow cell detachment but are inelastic materials.

We have created a cell culture platform that combines mechanical conditioning in vitro and then allows nondamaging detachment of cells and ECM for therapeutic use. Poly(N-isopropylacrylamide) is a thermally responsive polymer, thatwhen attached to culture surfaces, allows cell attachment at 37degC, and spontaneous detachment at room temperature, without using damaging enzymatic treatments. We have modified commercially available 6-well silicone plates with amine-conjugated surfaces, to incorporate PIPAAm to create an elastic substrate that can also change surface properties with temperature change.

PIPAAm was first copolymerized with 2% w/w acrylic acid (AAc), which was then conjugated with the amine-treated silicone surface through N,N'-dicyclohexylcarbodiimide chemistry. PIPAAm-co-AAc composition was verified using x-ray photoelectron spectroscopy (XPS) and acid titration. Phase transition temperature of PIPAAm-co-AAc is 30degC (vs 32degC for PIPAAm), which still works for cell culture. PIPAAm-co-AAc addition to the amine-treated silicone surface was verified using XPS and infrared spectroscopy (FTIR). Temperature change properties of the modified surface were verified through contact angle analysis.

30. Synthesis of Cyclic-Linear Diblock Copolymers of PEO and Polyesters

Gladys Rocio Montenegro-Galindo, B.S. and Coleen Pugh, Dr., Department of Polymer Science, The University of Akron, Akron, OH

Block copolymers composed of a poly(ethylene glycol) block and biodegradable polyester block have been used in the field of controlled drug delivery due to their biocompatibility and degradability. In order to minimize opsonization (i.e. foreign body targeting by hydrophobic proteins in bloodstream that leads to their elimination), different coating methods included PEGylation have been used. The goal of this project is to synthesize block copolymers with a cyclic poly(ethylene glycol) block and a linear polyester block using two polymerization methods: ring-opening polymerization of cyclic esters, such as ε-caprolactone using "3,4-(42-crown-14)benzyl alcohol" as the initiator and with tin octoate as the catalyst; and polycondensation of α-hydroxyacids, such as lactic acid, using "3,4-(42-crown-14)benzyl alcohol" as an end-capping agent. The linear block copolymer analogs will also be synthesized in order to compare the properties between the two types of architectures. Micro/nanospheres made out of these copolymers will be prepared and analyzed to determine their feasibility in controlled drug delivery systems. The lack of end groups in the PEG block may provide better coating to the hydrophobic core and encapsulated drugs against opsonization. The cyclic character of this block may also help the biodistribution of the particles due to the lower intrinsic viscosity of cyclic polymers compared to linear polymers.

Functional Materials: Membranes and Layered Systems (1)

Organizer: Peter Pintauro Vanderbilt University, Nashville, TN
Organizer: Jeffrey A. Gray Ohio Northern University, Ada, OH
Presider: Jeffrey A. Gray Ohio Northern University, Ada, OH
Presider: Peter Pintauro Vanderbilt University, N/a

Session Overview: This session will cover new membranes and structured (layered) materials for energy-related applications.

31. Proton Conducting Membranes From Electrospun Nafion Nanofibers

Kyung Min Lee[1], Jonghyun Choi[1], Ryszard Wycisk[1], Peter Pintauro[2] and Patrick Mather[3], (1)Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH, (2)Department of Chemical Engineering, Vanderbilt University, Nashville, TN, (3)Department of Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY

The concept of creating a proton conducting membrane from an embedded mat of electrospun ionomer nanofibers represents a novel "forced assembly" alternative approach to the use of block copolymers and polymer blends. We have been fabricating such membranes for hydrogen/air fuel cell applications. The fabrication process consists of the following three steps: (1) electrospinning an ionomer solution into a nanofiber mat, (2) compaction of the mat and interfiber welding, (3) filling the void space between fibers with inert matrix polymer to create a defect-free dense membrane.

We have recently reported on a nanofiber network proton conducting membrane that was prepared from sulfonated poly(arylene ether sulfons) (sPAES) nanofibers and a commercially available photocurable polyurethane matrix polymer**[1]**. This membrane exhibited a high proton conductivity, with good mechanical strength, moderate water swelling, and very low gas crossover, as compared to homogeneous, recast sPAES films.

More recent work has focused on the fabrication and characterization of composite membranes where the nanofibers are composed of perfluorosulfonic acid (e.g., DuPont's Nafion®). An overview of this work will be presented, including a detailed description of the membrane fabrication procedure. The effects of fabrication conditions (e.g., nanofiber diameter and nanofiber mat density) on the final membrane properties will be described and the possible use of perfluorinated ionomer nanofiber membranes in fuel cells will be discussed.

[1] J.Choi, K.M.Lee, R.Wycisk, P.N.Pintauro and P.T.Mather, Nanofiber Network Ion-Exchange Membranes, *Macromolecules*, **41(13)**, 2008, 4569–4572.

32. Novel Carbon-Siliocn Composite for Advance Lithium Battery

Maryam Nazri and **Gholam-Abbas Nazri**, Energy Storage Stystems, GM Research and Development Center, Warren, MI

Lithium battery is the most promising technology for electric-based transportation. The recent progress in this field has shown the potential of this technology to meet the requirements of a Plug-in and full electric vehicle in the near future. In this work, we propose to optimize an advance anode based on carbon-silicon composite with over an order of magnitude higher energy density than the current anode in lithium-ion technology. Our preliminary data in this area has shown significant enhancement of energy density and power capability of the carbon-silicon composite anode. This technology may enable future plug-in hybrid and full electric vehicle to have improved range and higher electric drive autonomy. In addition, the material used in this technology is low cost and abundant suitable for automotive application.

Among various alternative anode materials the C-Si composite has the highest gravimetric and volumetric energy density. It is the ultimate anode plate for advance batteries. In current lithium-ion battery, only one lithium atom can be stored for each six carbon to form LiC_6 compound delivering about 370 Ah/kg. In contrast each silicon atom can store over four lithium atoms to form a composition close to Li_4Si with energy density over 3000 Ah/kg. We have made significant improvement in electrode engineering of the carbon-silicon composite, and with further optimization this technology may replace current LiC_6 anode in lithium-ion technology.

33. Syntehsis and Properties of Layered Oxides

Gholam-Abbas Nazri, Energy Storage Stystems, GM Research and Development Center, Warren, MI

Synthesis and Properties of Layered Oxides

Gholam-Abbas Nazri

GM Research and Development Center, Warren, Michigan, USA

Layered oxides are promising materials for many technologically important applications. They are unique materials with isotropic characteristics. The metal oxide slabs can be modified through doping with cations and anions to change physicochemical properties of these materials. The interlayer spacing of these materials can be modified to incorporate ions, molecules, and polymers and provide a new class of molecularly mixed composites with properties that can't be achieved by mechanical mixing. The reactivity and energetic of the layered oxides can be changed dramatically by intercalation of highly electro-positive ions between the metal slabs.

In this talk several synthesis methods will be reviewed for preparation of doped layered oxides. Application of layered oxide for energy conversion devices and catalysis will be discussed.

General Catalysis (1)

Sponsor: Saint-Gobain NorPro
Organizer: Dave VanderWiel Saint-Gobain NorPro, Stow, OH
Organizer: Stephen Dahar Saint-Gobain NorPro, Stow, OH
Presider: Dave VanderWiel Saint-Gobain NorPro, Stow, OH
Presider: Stephen Dahar Saint-Gobain NorPro, Stow, OH

Session Overview: The General Catalysis Symposium will focus on novel catalytic materials for energy and environmental applications, including functional catalytic structures, adsorption & surface phenomena, catalysis in novel reaction systems, developments in gas-to-liquids catalyst materials, catalyst support materials, high selectivity catalysts, future trends in catalysis and related topics. Speakers will include academic and industry researchers, including invited talks from throughout the region.

34. Ordered Mesoporous Silica, Alumina and Carbon as Potential Catalysts and Catalyst Supports

Mietek Jaroniec, Department of Chemistry, Kent State University, Kent, OH

The self-assembly synthesis of ordered mesoporous silicas, which was reported in 1992, is considered as a major breakthrough in the area of nanomaterials. Since 1992 about thirteen thousands papers have been published on the synthesis, characterization and applications of ordered mesoporous materials (OMMs). Silicas, organosilicas, inorganic oxides, carbons, polymers and related organic-inorganic composites, prepared either by soft- or hard-templating strategies, become more and more important in many fields of science and technology such as adsorption, catalysis, separations, environmental processes, nanotechnology and biotechnology. One of the important potential applications of OMMs is to use them as catalysts or as catalyst supports for the incorporation of organic and/or inorganic catalytic species. Two major approaches have been used for introduction of these species into OMMs: (i) direct addition during one-pot synthesis, and/or (ii) post-synthesis incorporation. Both approaches alter the specific surface area, pore size, pore volume, pore accessibility and surface properties of the resulting OMM-supported catalysts in comparison to unmodified OMM materials. These issues are presented here with special emphasis on mesoporous silicas, aluminas and carbons.

35. DIRECT CH4 SOLID OXIDE FUEL CELL On Cu-Ni ANODE CATALYST

Steven Chuang, Dr, Felipe Guzman and Rahul Singh, Chemical and Biomolecular Engineering, The University of Akron, Akron, OH

The direct electrochemical oxidation of CH_4 was studied in a solid oxide fuel cell (SOFC) with a Ni and Cu-Ni anode electrocatalyst by measuring the performance characteristics (current-voltage curves) at 750 °C under steady state CH_4 and H_2 flow. The current-voltage curves for the Ni anode showed the maximum power density degraded from 0.1 to 0.02 W/cm^2 after 14 h of exposure to CH_4. In contrast, the current-voltage curves for Cu-Ni anode showed the maximum power density remained at 0.1 W/cm^2 after 120 h of exposure to CH_4. Examination of (i) the anode microstructure by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS), and (ii) anode electrochemical performance by voltage-current curves, revealed the addition of Cu improved the resistance to carbon formation on the anode. Development of an effective catalyst for the CH_4 SOFC requires a fundamental understanding of the mechanism of the electrochemical oxidation of CH_4 on the anode catalyst surface. This presentation will report results of an experimental study of the electrochemical oxidation of CH_4 on a Cu-Ni anode, focusing on the microstructure and performance characteristics (current-voltage performance) of Ni and Cu-Ni anode before and after a long term exposure of CH_4. The results of XRD and impedance spectroscopy for H_2 and CH_4 fuel will be discussed.

36. Novel Catalytic Metal Oxide Nanofibers

Sneha Swaminathan, Carl Loskofsky and George G Chase, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH

Nitrogen oxides (NO_2, NO) and Carbon monoxide (CO) are proven environmental and health hazards and their abatement is a topic of immediate concern. Noble metal oxide nanofibers are potential candidates as catalysts for such heterogeneous catalytic reactions. These nanofibers have special electronic and morphological properties as well as high surface energy which result in their unique catalytic activity/selectivity. The noble metals which constitute palladium, platinum and rhodium have been incorporated into alumina nanofiber by sol gel processing and electrospinning techniques. Electrospinning is a process in which fibers of nanoscale or submicron scale are generated, as the electrified jet (composed of a highly viscous polymer solution) is continuously stretched due to electrostatic repulsions between the surface charges and the evaporation of solvent. The diameters of the nanofibers and nanoparticles were in the range of 60-100nm and 2-7nm, respectively. Using the vacuum molding technique, the catalytic nanofibers were incorporated into an alumina micro-fibrous filter which was used in experiments to test the nanofiber performance. These materials have been successful in converting NO to N_2 and CO to CO_2. The efficiency of the catalytic fibrous filter was similar to a commercial catalytic converter. These nanofibers have also been used to catalyze liquid phase reactions.

37. The Catalyst Is Not Consumed Because the Catalyst Is An Electric Field with a Fractional Charge

Ralph A. Gardner-Chavis, Cleveland State University - Emeritus, Cleveland, OH

The Atomic Energy Level, AEL, tables from NIST present energy states that electrons may occupy upon being excited from a bound state. Examples: the first state above the ground state of the chromium atom is at 7,593.16 cm^{-1}. The first state for the chromium positive ion is at 11,961.81 cm^{-1}. The first four states for the chromium double positive ion are at 62.22, 183.16, 356.55 and 576.08 cm^{-1}. **States this close to the ground state will be occupied for a fraction of time,**

producing an electric field with a fractional charge. Each positive ion possessing catalytic activity has a different set of these low-lying states, thus each ion presents an electric field with a different fractional charge to prepare the chemical reactants for the catalytic event. The appropriate ion to catalyze a chemical reaction has the field with the fractional charge which when imparted to the two reactants, changes the frequencies of the fields of the reactants at the sites of reaction so that they match harmonically, i.e. the ratio of the frequencies is a power of two. **When the reactants meet in the field, because the frequencies of the electric fields now match, resonance occurs. It is during resonance that electrons are exchanged and chemical bonds are broken and made to satisfy the Free Energy constraint**. Examples: oxidation of CO by gold or zinc oxide, chlorination of CO by chromous ion and the difference in reaction between zinc carbonic anhydrase and cobalt and cadmium homologues.

Inorganic Chemistry: General

Sponsor: ACS Division of Inorganic Chemistry
Organizer: John Protasiewicz Case Western Reserve University, Cleveland, OH
Presider: Scott D. Bunge Kent State University, Kent, OH

Session Overview: This session is for contributed talks in the broad area of Inorganic Chemistry

38. Low Power Photon Upconversion

Tanya N. Singh-Rachford and Felix N. Castellano, Department of Chemistry & Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH

Photon upconversion, a phenomenon based on sensitized triplet-triplet annihilation (TTA) continues to emerge as a promising wavelength-shifting technology. The sensitized TTA mechanism allows nonlinear upconversion to become linked to sequentially highly allowed one photon absorptions, thereby allowing the use of low power excitation sources. Various highly photo-stable metal-organic chromophores in conjunction with appropriate acceptors/annihilators have been explored which span the near-IR to near-visible region of the spectrum. Visualization of this phenomenon in solution and in a variety of solid polymer films highlighting upconversion processes at low excitation power, including appropriately filtered solar photons. Generalized molecular design constraints and measurement techniques applied to these low power nonlinear processes will be described.

39. Chlorophosphazenes, Their Lewis and Bronsted Acid-Base Chemistry and Potential Involvement of Superacids in the Problems Relating Their Syntheses and Storage

Zin-Min Tun, Matthew J. Panzner, Doug Medvetz, Wiley J. Youngs and Claire A. Tessier, Department of Chemistry, University of Akron, Akron, OH

The main route to functionalized phosphazene polymers is by replacing the chloro-groups on the chlorophosphazene polymer with the desired side groups. One of the synthetic procedures to the parent chlorophosphazene polymer is the ring-opening polymerization (ROP) of $[PCl_2N]_3$. However, the ROP process is inefficient and irreproducible. To study the mechanism of the ROP, we focus on the fundamental acid-base chemistry of $[PCl_2N]_3$. $[PCl_2N]_3$ is a weak base and its reaction with relatively strong Lewis acids gave adducts $[PCl_2N]_3{\cdot}MX_3$ (MX_3 = $AlCl_3$, $AlBr_3$, $GaCl_3$) under rigorous anaerobic conditions and superacid adducts $[PCl_2N]_3{\cdot}HMX_{m+1}$ (HMX_{m+1} = $HAlCl_4$, $HAlBr_4$, $HGaCl_4$, $HSbCl_6$) in the presence of stoichiometric quantity of water or HX. Because $[PCl_2N]_3$ was synthesized from PCl_5, PCl_5 impurities can still be present in the ROP process. PCl_5 is a weak Lewis acid and it reacts with trace amount of water to give the marginally stable, $HPCl_6$. The presence of $HPCl_6$ in the ROP process might be responsible for the irreproducibility of the process. To understand the chemistry of $HPCl_6$, the more stable superacid adducts were characterized by X-ray crystallography, and variable-temperature NMR studies.

40. New Titanium Imido Complexes Utilizing Chelating Orthometallated Imine Ligands

John F. Beck and Joseph A. R. Schmidt, Chemistry, The University of Toledo, Toledo, OH

The use of orthometallated imines as ligands for late transition metals is well established. However, their use with early transition metals has been limited. This is to due to the inability of the aryl imine to undergo the necessary C-H activation with early transition metals. In order to synthesize early transition metal complexes that utilize orthometallated imines, our imines are activated prior to transition metal complexation with n-butyllithium though a regiospecific lithiation exclusively at the `ortho` position. The lithiated imine can then be reacted with early transition metal precursors to form the final orthometallated imine. This methodology was used to synthesize a series of `bis`-ligated titanium imido complexes. The reaction of two equivalents of Li-L with Ti(NR)Cl_2py_3, where R = aryl, alkyl, yielded highly symmetrical base free complexes of a distorted square pyramidal geometry. A `mono`-ligated imido complex was synthesized by the reaction of one equivalent of Li-L with a more sterically demanding aryl imido titanium species. However, when an alkyl imine was used, an inseparable mixture of isomers in rapid equilibrium was observed in solution with one equivalent of pyridine coordinated `trans` to the imido group.

41. Ancillary Ligand and Ketone Substituent Effects On the Rate of Ketone Insertion Into Zr-C Bonds of Zirconocene-1-Aza-1,3-Diene Complexes

Jie Zhang[1], Jeanette A. Krause[1], Kuo-Wei Huang[2] and Hairong Guan[1], (1)Department of Chemistry, University of Cincinnati, Cincinnati, OH, (2)National University of Singapore, Singapore

Zirconocene-1-aza-1,3-diene complexes, [Me2Si(C5H4)2]Zr[N(Ar)CH=CHCH(Ph)] (Ar = Ph: **2a**; Ar = `p`-MeOC6H4: **2b**) and Cp2Zr[N(Ar)CH=CHCH(Ph)] (Ar = Ph: **3a**; Ar = `p`-MeOC6H4: **3b**), have been synthesized and characterized. X-ray crystal structure determination of compounds **2a**, **3a**, and **3b** reveals folded five-membered ring moieties for the zirconacycles. DFT calculations and variable temperature NMR experiments for complex **2a** establish a rapid ring-flipping process at room temperature, with the conformation bearing a pseudoequatorial Ph group more stable by 5.6 kcal/mol. Kinetic studies on ketone insertion into these zirconocene complexes show second-order reactions, and the insertion is more favorable in the presence of a [Me2Si] `ansa` bridge, a less electronrich substituent on the nitrogen, and a more basic ketone. One of the insertion products, namely Cp2Zr[N(Ph)CH=CHCH(Ph)CPh2O] (**5a**), has also been characterized by X-ray crystallography.

42. Reactivity of (3-Iminophosphine)Palladium(II) Complexes: Evidence of Hemilability

Andrew Shaffer and Joseph A. R. Schmidt, Department of Chemistry, The University of Toledo, Toledo, OH

Several palladium(II) 3-iminophosphine complexes were synthesized in moderate to high yield. With relevance to many palladium-catalyzed coupling reactions, these complexes incorporate a wide variety of ligands, including amines, alkyls, allyls, and triflates. The presence of both eta.1- and eta.2-coordination modes demonstrates the hemilability of the 3-iminophosphine ligand class, as determined by X-ray crystallography and NMR spectroscopy.

Plenary Lecture: Professor Charles M. Lieber of Harvard University

Organizer: Kenneth W. Street The NASA-Glenn Research Center, Cleveland, OH

43. Nanowires: A Platform for Nanoscience and Nanotechnology

Charles M. Lieber, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA

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Poster Session (1)

Organizer: Mike Nichols John Carroll University, University Heights, OH
Organizer: Mark J. Waner John Carroll University, Cleveland, OH

Session Overview: Poster topics are in the general areas of: Biochemistry, Bioorganic, Physical and Analytical Chemistry, Chemical Education and Electrochemistry

44. Structural and Electronic Characteristics of Human Islet Amyloid Polypeptide (hIAPP) Leading to Aggregate Formation

Gholamreza Eizadkhah and M. C. Milletti, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI

Aggregation of the human form of Islet Amyloid Polypeptide (IAPP) is thought to cause membrane disruption in pancreatic β cells. Subsequent fibrilization causes the formation of amyloid deposits that are associated with Type II diabetes. In contrast, the rat form of IAPP does not undergo the same process and Type II diabetes has not been observed in rats. Structural studies of hIAPP have shown that the 20-29 segment of this peptide plays an essential role in the aggregation process. In this work we use Density Functional methods to compare the structural and electronic characteristics of human and rat IAPP in order to determine which features lead to aggregation. Optimized structures at the B3LYP/3-21G level of theory have been determined for the human and rat forms of the 20-29 segment of IAPP. While hIAPP exhibits a mostly linear structure with a slight bend at the Phe^{23} residue, the 20-29 segment of rIAPP is completely folded onto itself. This key structural difference is driven by the formation of several intramolecular hydrogen bonds in the rat form. Calculations on dimers of these segments further support the finding that hydrogen bonds are responsible for the observed structural differences: in the human form several hydrogen bonds are formed between the two fragments, while in the rat form the preexisting intramolecular interactions prevent aggregation between fragments.

45. An All Purine Sequence within the 5'-UTR of the MT3 Matrix Metalloproteinase mRNA Forms An Extremely Stable G-Quadruplex and Represses Translation in Mammalian Cells

Mark Morris and Soumitra Basu, Department of Chemistry, Kent State University, Kent, OH

MT3-MMP is a matrix metalloproteinase and one of the important components in the regulation of cancer cell invasion and metastasis. Interestingly, the MT3-MMP mRNA contains a 20 nucleotide purine-only G-rich region (M3Q) upstream of its initiation codon. Herein, we report that the M3Q sequence has an inhibitory role on translation of a reporter gene in eukaryotic cells most likely via formation of a stable intramolecular G-quadruplex structure. Formation of the quadruplex structure was done by circular dichroism (CD) spectroscopy and enzymatic footprinting with RNase T1. CD-melting showed the unusual stability of the quadruplex when addition of only 1 mM KCl resulted in a 30°C increase in the melting temperature (Tm) compared to that obtained in the absence of added salt. Additionally, the M3Q motif present in the context of the entire 5'-UTR of MT3-MMP repressed activity of its downstream gene by more than half in a dual luciferase reporter assay performed in HeLa cells. This report is the first to establish a functional role of a quadruplex forming sequence within the MT3-MMP 5'-UTR in the regulation of translation in mammalian cells and to our knowledge shows that the M3Q sequence forms one of the most stable, naturally occurring, intramolecular RNA quadruplexes.

46. Loop Complimentarity Affects Quadruplex Conformation and Insulin Binding Ability in G-Quadruplexes Formed by ILPR Repeats

Joseph Schonhoft, Arijit Das, Firehiwot Achamyeleh, Sheema Samdani, Hanbin Mao and Soumitra Basu, Department of Chemistry, Kent State University, Kent, OH

The Insulin Linked Polymorphic Region (ILPR) is a VNTR region located upstream of the Insulin (INS) gene composed of the majority repeat ACAGGGGTGTGGGG (repeat a), along with several other polymorphisms (repeats b-k). Here, we have characterized the ability of G-quadruplexes formed from the most common repeat sequences (a-d) to bind the protein Insulin, which was previously shown to bind a G-quadruplex formed by the tandem repeat of two ‘a’s (‘aa’). All of the sequences form intramolecular G-quadruplexes, based upon circular dichroism spectra and their mobility in native gel. Our findings indicate that the repeat ‘a’ G-quadruplex exhibits the strongest binding to Insulin over G-quadruplexes formed by other ILPR repeats tested and it appears Insulin prefers to bind to quadruplexes with an antiparallel conformation. Additionally, linker regions of repeat ‘a’ (ACA:TGT) with a Watson-Crick (WC) relationship seemingly play an important role in favoring a specific G-quadruplex conformation, and based on our data is necessary for binding. Interestingly, binding to Insulin is reduced in sequences lacking the WC complimentarity and when the WC complimentarity in the putative loops is restored the binding also recovers. Finally, combining data from a DMS footprinting assay with binding affinities obtained for ILPR mutants we identify a specific nucleotide that is critical for binding. Collectively, our results illustrate the specific nature and fundamental characteristics of Insulin binding to the ILPR G-quadruplex, which is unique among current examples of protein-quadruplex interactions.

47. Novel Synthetic Inhibitors of 3-Hydroxy-3-Methylglutaryl-Coenzyme A (HMG-CoA) Reductase Activity That Are Structurally Unrelated to Existing Statins

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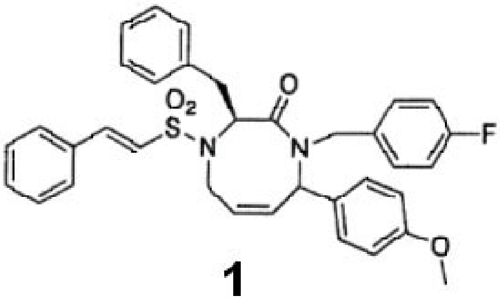

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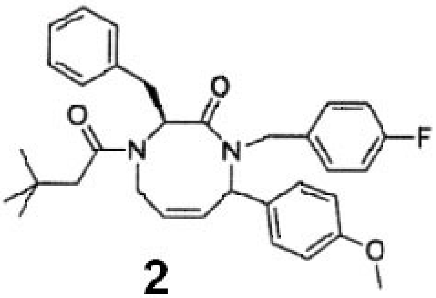

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Pilot-scale libraries of 131 eight- or nine-membered medium ring lactams (MRLs) and related tricyclic compounds (either lactams, thiolactams or amines) were screened for their ability to inhibit the catalytic activity of human recombinant HMG-CoA reductase `in vitro`. A dozen of synthetic compounds, including **1** and **2**, mimic the inhibition of purified HMG-CoA reductase activity caused by pravastatin, fluvastatin and sodium salts of lovastatin, mevastatin and simvastatin in this cell-free assay, suggesting direct interaction with the rate-limiting enzyme of cholesterol biosynthesis. Moreover, several MRLs inhibit the metabolic activity of L1210 tumor cells `in vitro` to a greater degree than fluvastatin, lovastatin, mevastatin and simvastatin, whereas pravastatin is inactive. Although the correlation between the concentration-dependent inhibitions of HMG-CoA reductase activity over 10 min in the cell-free assay and L1210 tumor cell proliferation over 4 days in culture is unclear for this series of bioactive compouds, **1** and **2** elicit interesting combinations of statin-like (IC_{50}: 7.4-8.0 μM) and anti-tumor (IC_{50}: 1.4-2.3 μM) activities. The HMG-CoA reductase-inhibiting activities of pravastatin and **1** persist in the presence of increasing concentrations of NADPH. But increasing concentrations of HMG-CoA block the HMG-CoA reductase-inhibiting activity of pravastatin without altering that of **1**, suggesting that MRLs and existing statins may have different mechanisms of enzyme interaction and inhibition. When tested together, suboptimal concentrations of synthetic MRLs and existing statins have additive inhibitory effects on HMG-coA reductase activity. Preliminary molecular docking studies with MRL-based inhibitors indicate that these ligands fit sterically well into the HMG-CoA reductase statin-binding receptor model.

48. The Bioaccumulation and Toxicity of Silver Nanoparticles in Animal and Plant Tissues

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Silver nanoparticles (AgNPs) are currently receiving considerable attention because of their numerous applications in biology, pharmacy, and medicine. However, very little is known about their bioaccumulation and toxicity in living organisms. Animal model: To examine these aspects, developing chick embryos were injected twice with AgNPs (borohydride-reduced, 5-20 nm) solutions of various concentrations. Embryos' organs, blood, and tibiotarsus were harvested on the 20th day of incubation and examined. Plant model: Tomato, bean, and lettuce seeds were germinated in culture media of various concentrations of AgNPs. The AgNPs accumulation in plant and animal tissues was quantified by GFAAS spectrometry on ground tissue powder. The DNA and oxidative damage in tissues was determined using a Comet and glutathione peroxidase assay, respectively. The hematological analysis revealed the relationship between white blood cells counts and AgNPs treatment.

49. Quadruplex Conformation Dictate the Binding of the Malachite Green Analogs to ILPR DNA

Katherine I. Poinski, Mark Morris, Lionel Sanguinet, Jarrod Williams, Robert Twieg and Soumitra Basu, Department of Chemistry, Kent State University, Kent, OH

Guanine-rich nucleic acid sequences can adopt non-canonical structures called G-quadruplexes. The insulin-linked polymorphic region (ILPR), located upstream of the insulin gene is very G-rich, and has been linked to the insulin dependent diabetes mellitus (IDDM) or juvenile diabetes (type I diabetes). The ILPR is composed of a 14-15 base tandem repeat sequence, the most prevalent being $(ACAGGGGTGTGGGG)_n$, which has been shown to form a G-quadruplex `in vitro`. The ILPR may affect expression of the insulin gene, and it is suggested that stabilization of the ILPR via quadruplex or higher order structure can have a positive impact on insulin expression. Thus, agents that may stabilize such structures can be envisioned to have a therapeutic role, as it can lead to enhanced insulin production. Therefore, it is hypothesized that small-molecule binding may regulate the role of ILPR DNA, in turn affecting insulin production. Recently, the triaryl dye malachite green has been shown to preferentially bind to quadruplex DNA over duplex DNA. We have investigated a series of malachite green analogues using UV-Vis and fluorescent spectroscopies to evaluate the affinity of these ligands to ILPR. At least three of the analogues showed 2-3 fold tighter binding compared to malachite green. At least two compounds from the about dozen compounds tested, including malachite green, showed cooperative binding. Brilliant Green showed 10 fold preferential binding to the all parallel form of the ILPR as compared to double stranded DNA. The studies lay the groundwork for establishing structure-activity relationship of the triaryl dyes with the G-quadruplexes.

50. SAR Study of the Effect of PTB Analogues On the Maillard Reaction Radical Pathway

Wei Shen and Roger Lloyd, Department of Chemistry, The University of Memphis, Memphis, TN

Products of Maillard reaction undergo a variety of reactions to irreversibly crosslink amino acid residues, particularly lysine and arginine, to form advanced glycation endproducts (AGEs). In long-lived tissue proteins, such as lens albumin, these AGEs accumulate as a function of time, and at an increased rate in diabetics due to elevated blood glucose level. The formation of crosslinks causes proteins to lose flexibility and to become rigid, which along with other effects, plays a major role in the development of circulatory complications in diabetes and aging. Tremendous effort has been devoted to finding Maillard reaction inhibitors . Many small molecules have been designed to effectively interfere with or even reverse the Maillard reaction to give promising anti-AGE results.

The Maillard radical pathway occurs in early glycation stage. Inhibition of Maillard radical pathway can presumably stop the Maillard reaction at early step, thus preventing the formation of AGE and occurrence of the Maillard reaction related diseases. PTB is a small molecule alleged to prevent the formation of AGE by selectively cleaving the carbon-carbon bond of Amadori-dione from which both the Maillard radical and AGE were formed. They could even reverse neurovascular effects of diabetes by converting Amadori-dione back into amino acid or peptide. Given the significant inhibitory effect of PTB on the Amadori-dione in early stage of Maillard reaction, we suggest that PTB analogue should affect the radical pathway as well.

In this paper, we report the synthesis of libraries of PTB analogues and the SAR study of the effect of these analogues on Maillard reaction radical pathway.

51. Routes to Platinum(IV) Antitumor Compounds

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Organoplatinum antitumor drugs, principally Cisplatin and Carboplatin, have been hugely successful for the treatment of a range of cancerous disease. These compounds, and other like them, are platinum(II) compounds. Recently, there has been interest in the preparation of platinum(IV) compounds that might display antitumor properties. It has been reported that oxidation of Cisplatin with nitric oxide generates an active species that can be trapped with various ligands to generate platinum(IV) compounds which display good antitumor activity. This approach would seem to be unreliable at best. It is not reproducible and generally leads to the formation of several products. A potentially better approach involves the treatment of Cisplatin with hydrogen peroxide to generate the corresponding (dihydroxo)platinum(IV) compound. The hydroxyl groups provide reactive functionality that permits the attachment of a variety of organic fragments.

52. SIRT1 Processing of N(epsilon)-Acetyllysine Analogs

Nuttara Jamonnak, **Brett M. Hirsch**, Yi Pang and Weiping Zheng, Department of Chemistry, University of Akron, Akron, OH

Peptides containing L-N(epsilon)-acetyllysine (L-AcK) or its analogs were prepared and employed to study the substrate specificity of human SIRT1 (a Sir2 family enzyme) at its active site. Our results suggested that the SIRT1 active site exhibited (i) a stereospecific recognition of L-AcK versus its D-isomer and (ii) a very stringent requirement for the distance between the alpha-carbon and the side chain carbonyl oxygen, with that found in L-AcK being optimal for SIRT1 substrate processing. Besides having a direct impact on developing inhibitors for the therapeutically important human SIRT1, our current study may have also furthered our understanding of the substrate specificity of Sir2 enzymes in general.

53. Investigation of Cofactor Dependent Nucleic Acid Enzymes

Eduardo Paredes and Subha R. Das, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA

The glmS riboswitch occurs in all gram-positive bacteria to control the overproduction of glucosamine-6-phosphate (GlcN6P). Recent structural analyses and biochemical studies suggest that the small molecule GlcN6P binds to the RNA and catalyses a site-specific RNA cleavage. Through analyses of both normal and 5'S-hyperactivated RNA substrates, and differing cofactors, we are investigating the role of the putative GlcN6P cofactor. We have also used `in vitro` selection to identify GlcN6P-dependent DNAzymes to investigate the role and efficiency of a cofactor. Once optimal sequences are identified that cleave RNA substrate, we plan to examine the reaction mechanism with the use of 5'S-hyperactivated substrate. These studies would permit the comparison of reaction mechanisms to uncover the role of a cofactor, in different nucleic acid systems. Another selected DNAzyme, the HD3 DNAzyme that uses L-histidine as a putative cofactor is also being studied with the use of 5'S-hyperactivated substrate and differing cofactor, to uncover its mechanism.

54. Aspirin and Breast Cancer: Studies IN Mice

Vinay Likhite and William D. Bush, Breast Cancer Research, Baroda Cancer Research Center, Plattsburgh, NY

More than 80 million aspirin (acetyl salicylic acid) tablets are consumed each day in the United States to control fever and pain and for the reduction in mortality from cardiovascular disease and possibly colorectal cancer. Observational studies reporting a protective effect of aspirin on breast cancer have been mixed. Recently Terry et al [JAMA 291(20), 2433-2440,2004] have presented statistical data, supported by other epidemiologic and laboratory evidence, to bolster their case for the use of aspirin as chemopreventive agents against breast cancer. Recent comparison of mouse and human genomes indicates that humans are genetically remarkably close to the lab mouse, and that 98% of the genes in humans have an exact match to those in the mouse. These findings bolster the notion that the mouse remains an excellent model for the study of breast cancer in general. Female C3H/Lk mice develop mammary adenocarcinomas spontaneously, and have done so consistently for over 70 inbred generations in our laboratory. In 2004 we initiated a study to determine if oral administration of aspirin has any effect on the incidence of these tumors. To date, of the 49 females receiving aspirin 42 have developed the tumors. On the other hand, of the 40 controls 36 have developed the tumors. That is, the incidence of the mammary adenocarcinoma is the same in both the experimental and control mice. These results clearly demonstrate that daily ingestion of aspirin does not prevent the appearance of breast cancers in C3H/Lk mice. (Supported by Champlain Valley Immunology Foundation grants.)

55. Hormones and Breast Cancer: Studies in Mice

Vinay Likhite, Breast Cancer Research, Baroda Cancer Research Center, Plattsburgh, NY

Female mice of the C3H/Lk strain develop breast cancer spontaneously. But the males of this strain do not, and remain cancer-free for their entire lives. We theorized that the failure of these cancers to appear in the males might be due to the presence of androgens, and that these hormones might also have a similar effect in the females. To test this hypothesis we treated a group of 48 one-month-old females with the androgen testosterone [100 micrograms of depo-testosterone [(Upjohn)/female/month)] and observed them weekly for their entire lives for the development of breast cancer. <u>None</u> of these females developed breast cancer and they remained cancer-free for their entire lives. In contrast, <u>all</u> of the females in a large (209) group of controls developed the breast cancer: 15% by 4 months of age, 94% by 9 months of age, and almost 100% by 15 months of age. Administration of the hormone to females in whom the breast cancer had already appeared did not arrest, delay or reverse the progression of the cancer. The mechanism of the androgen mediated prevention of breast cancer in the C3H/Lk female

mice remains unknown. And the potential for testosterone (or its analogs) as a preventive treatment for breast cancer in women, especially in those with a family history of breast cancer, remains a distinct but as yet untested possibility. (Supported by grants from the Champlain Valley Immunology Foundation).

56. Synthesis of Glucosamine-6-Phosphate (GlcN6P) Analogues to Examine Molecular Recognition and Mechanism of the Glms Ribozyme

Joy K. Maity, Tao Han and Subha R Das, Chemistry Department, Carnegie Mellon University, Pittsburgh, PA

The glmS RNA is conserved in all gram-positive bacteria and acts as a 'riboswitch' to bind the metabolite glucosamine-6-phosphate (GlcN6P) and activate RNA cleavage. Thus the glmS riboswitch is a ribozyme that depends on the small molecule GlcN6P. Although GlcN6P or its analogue glucosamine-6-phosphate (GlcN6P) is observed in the binding pocket in recent crystal structures of the glmS RNA, the basis for molecular recognition of GlcN6P and its mechanism of action remains unclear. To examine the determinants of GlcN6P molecular recognition and to investigate the glmS RNA cleavage mechanism we have synthesized various analogues GlcN6P modified at the 3-position. Starting from N-acetyl-D-glucosamine the 3-β-hydroxyl was inverted displaced and reacted further to obtain the chloro-, azido-, amino- or hydrido- substituted analogues. These GlcN6P analogues will be useful as probes for the glmS ribozyme cleavage mechanism as well as potential agonists and glmS riboswitch targeting antibacterial agents.

57. Photolabile Protecting Groups for Caging the 2'-Hydroxyl in Modified RNA

Tao Han, Joy K. Maity and Subha R Das, Chemistry Department, Carnegie Mellon University, Pittsburgh, PA

Nucleic acids that are ‘caged’ with photolabile protecting groups are very useful for investigating nucleic acid dependent processes and biological functions. In order to ‘cage’/protect the 2′-hydroxyl of RNA in a sequence specific location, a photolabile protecting group that is stable under the conditions required for solid phase RNA synthesis and deprotection can be used. Here we describe the syntheses of nucleosides protected with a family of photolabile protecting group based on the 2-nitrobenzyl group. The synthesis of 2′-O-(2-nitrobenzyl)adenosine, 2′-O-(2-nitro benzyl)inosine, 2′-O-(2-nitrobenzyloxymethyl)adenosine and 2′-O-(4,5-dimethoxy-2-nitrobenzyloxy methyl) adenosine have been accomplished based on previous reported and newly developed procedures. The 2′-O-(2-nitrobenzyl) nucleosides have been used in RNA solid phase synthesis and tested for UV deprotection conditions. The other 2-nitrobenzyl analogues will be compared with 2-nitrobenzyl to find out the photolabile protecting group with highest efficiency in both UV cleavage and solid phase synthesis. Nucleosides with 2′-hydroxyl photolabile protecting groups are expected to provide access to sensitive as well as previously hard to obtain modified nucleic acids such as 5′-phosphorothiolate RNAs and branched nucleic acids.

58. Fluorescence Enhancement of Adenine and Other Purines: Applications in Enzyme Kinetics

Dan N. Bigman[1], Edwin Quiñones[2] and Cristina Padilla[1], (1)Department of Chemistry, University of Puerto Rico, San Juan, PR, (2)Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, Rio Piedras, PR

Nucleic acids have intrinsically very low room-temperature fluorescence. By means of the addition of a heavy-atom containing molecule, 3-bromopropan-1-ol, we have been able to significantly enhance the fluorescence of adenine, 6-methylpurine and 7-methyladenine. In contrast, other nucleic acids such as adenosine and hypoxanthine did not exhibit this effect. We determined that 3-bromopropan-1-ol and adenine form a 1:1 interaction. Enhanced fluorescence as a function of temperature was likewise studied, showing a linear relationship with temperature. A second aspect of this work strives to explore applications of this phenomenon. We studied the conversion of adenine to hypoxanthine as catalyzed by the enzyme adenosine deaminase (ADA). This enzyme catalyzes the removal of the amino group, replacing it with a hydroxyl. Standard assays rely on HPLC, which is a discontinuous method, or UV-Vis spectroscopy, in a region which both adenine and hypoxanthine absorb. We take advantage of the non-fluorescence of hypoxanthine, which permitted us to use the decrease in fluorescence of adenine as a function of time with the purpose of studying reaction kinetics. We confirm the products using HPLC in the end solution. There is interest in the activity of ADA due to its involvement if key metabolic pathways related to the immune system. In this work we report kinetics parameters obtained.

59. Withdrawn.

60. Chemical Selective Liposome Surface Functionalization through Staudinger Ligation

Hailong Zhang, Yong Ma and Xue-long Sun, Chemistry, Cleveland State University, Cleveland, OH

Liposome surface functionalization with biomolecules facilitates enormous potential applications of liposomes such as targeted drug and gene delivery. Several chemical modification methods, such as using amide or thiol-maleimide coupling as well as by imine or hydrazone linkage, have been developed. However, in many cases there is a lack of specificity resulting in the uncontrolled formation of the number of covalent bonds between liposome and biomolecules of interest. Most recently, Click chemistry has been investigated as it can occur efficiently and selectively between azide and alkyne in aqueous media. However, the key limitation of the Click chemistry is the use of Cu (I) catalyst, which results in residual copper in the liposome and could be a potential concern for liposome application. The Staudinger ligation, in which an azide and triphosphine selectively react to form an amide has been used for chemical selective modification of recombinant protein and cells without physiological harm. Herein, we report an efficient and chemical selective liposome surface functionalization with carbohydrate through Staudinger ligation. The effect of reaction conditions on the size and stability of liposome were investigated by dynamic light scattering and the leakage of entrapped 5, 6-carboxyfluorescein, respectively. Furthermore, the density and accessibility of grafted carbohydrate residues on the surface of liposome were evaluated.

61. Chemical Selective Liposome Surface Functionalization and Immobilization

Yong Ma, Hailong Zhang and Xue-long Sun, Chemistry, Cleveland State University, Cleveland, OH

Surface-immobilized liposomes are of interest for various potential applications, such as sensor and localized drug delivery, but their synthesis is challenging. Conventional liposome immobilization method involves the initial synthesis of the key anchor lipid, followed by formulation of the liposome with all lipid components. In this direct liposome formation method, some of the valuable anchor groups inevitably are facing the enclosed aqueous compartment and thus become unavailable for their intended immobilization use. Particularly, it is unrealistic if the anchor ligand is only available in minimum amount. Furthermore, anchor-lipid conjugates normally have limited solubility and stability in solvent, or are incompatible with various stages of preparation. Herein, we report an efficient and chemical selective liposome surface functionalization and immobilization method through Staudinger ligation. The liposome immobilization was investigated by synthesizing biotinylated liposome, which is immobilize onto streptavidin-coated glass slide, and by directly immobilizing onto azide functionalized glass slide through Staudinger ligation, respectively. The surface-immobilized liposomes are analyzed with AFM and fluorescent imaging techniques.

62. Synthesis of Open-Chain Epothilones

Sara Fedorka, Brice Baars, Hanan Haymour, Nick Maurer and Liyanaaratchige Tillekeratne, Department of Medicinal and Biological Chemistry, College of Pharmacy, University of Toledo, Toledo, OH

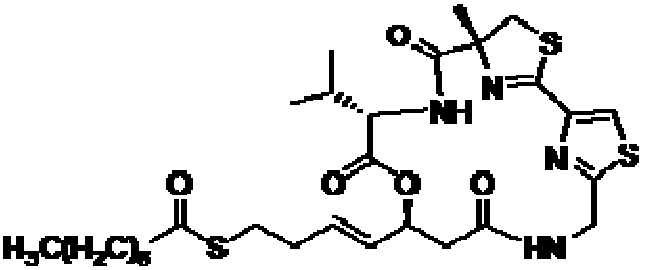
Epothilones are a class of naturally-occurring antitumor compounds. They are microtubule stabilizing agents that exert their anti-proliferative activity by disrupting microtubule dynamics, leading to arrest of cell division at G2/M phase and inducing apoptosis. These macrolactone anti-mitotic agents are similar to the clinically used anticancer drug paclitaxel in their mechanism of action. However, unlike paclitaxel, epothilones are effective against multiple drug resistant cell lines.

We have designed and synthesized a new class of open-chain epothilone analogues that retain some of the key structural elements known to be crucial for the biological activity of epothilones. Changes were effected mainly in the aromatic side chain while maintaining the minimum structural requirements necessary for biological activity. The two biologically important sectors were tethered via a small molecular scaffold. The synthesis of these open-chain epothilone analogues for SAR studies will be presented.

63. Synthesis of the Potent Anticancer Agent Largazole and Its Analogs

P.R. Bhansali and Liyanaaratchige Tillekeratne, Department of Medicinal and Biological Chemistry, College of Pharmacy, University of Toledo, Toledo, OH

Identification of new pharmacophores is an important paradigm in the development of anticancer agents with novel mechanisms of action and selective activity on cancer cells and minimal toxicity to other tissues. Natural products have been a consistent source of molecules of diverse structure and novel pharmacophores. A new anticancer natural product, largazole, with potent and selective activity on highly invasive transformed human mammary epithelial cells (MDA-MB-231) and transformed fibroblastic osteosarcoma (U2OS cells) by inhibiting Class I Histone Deacetylase was reported recently.



The identification of the structural elements responsible for the selective activity of largazole requires a detailed structure-activity relationship (SAR) study. Synthesis of largazole and its analogs for SAR studies will be presented.

64. Study of the Thermal Behavior of Sugar Solutions Using Differential Scanning Calorimetry

Ermias Gebremichael[1], Kenneth Alexander[1] and Alan Riga[2], (1)Industrial Pharmacy, University of Toledo, Toledo, OH, (2)Department of Chemistry, Cleveland State University, Cleveland, OH

Both the pharmaceutical and food industry have faced fundamental challenges related to the thermal behavior of excipients, in particular sugars, which are used in the production process. The heating and cooling of sugars can produce physical and chemical transformations that can be studied using Differential Scanning Calorimetry(DSC). The main goal of this study was to evaluate the thermodynamic properties of different sugar solutions and compare them to the pure sugar samples upon heating and cooling.
The sugars investigated include Amylose, Levulose, Mannitol, β- lactose, Dextrose hydrous, and α-lactose. A fixed concentration (20% w/v) was prepared for these sugars. Samples were placed in 100 μl aluminum pans. The pans were sealed hermetically and placed in a DSC. The temperature

range was between -60 ºC to 180 ºC at a heating and cooling rate of 10 ºC/min. The pure sugar samples ranged between 4-6 mg and were evaluated under similar conditions.All the sugar samples showed different DSC curves. The sugar solutions, and the pure sugar samples, showed on endothermic peak related to the heat of fusion.The exothermic phenomenon was not observed except for the mannitol solution.The thermodynamic properties of sugars upon cooling and heating vary based on the physical forms of the evaluated sugars, as well as the type of sugar. Some of the evaluated sugar solutions have shown three endothermic peaks and most of them don't show any exothermic peaks. This study provides fundamental information on the physical and chemical properties of the excipients in particular sugars during processing and storage.

65. Pharmaceutical Solid Dispersions: A Study of Their Physicochemical and Dissolution Characteristics

Ranajoy Majumdar, Kenneth S Alexander and Alan Riga, Pharmacy Practice, The University of Toledo, Toledo, OH

This study proposes to formulate ternary solid dispersion granules and to investigate their physicochemical and dissolution characteristics after preparation and upon storage for four weeks at 40^{0}C/75% RH. Ternary solid dispersions were prepared by hot-melt granulation in which the drug, Ibuprofen was dispersed in a molten dispersion carrier and coated onto an adsorbent. Polyethylene Glycol 8000® and Gelucire 50/13® were used as the dispersion carriers and Neusilin US2® was used as the surface adsorbent. Various complimentary techniques such as DSC, XRD, FTIR and UV spectrometry were used to investigate the physicochemical and dissolution characteristics of the drug at different times. Dissolution rate of Ibuprofen was slightly enhanced from the granules in some formulations upon storage for 2 and 4 weeks. The mechanism for further increase in drug dissolution from the solid dispersion granules is supposed to involve hydrogen bonding between the drug and Neusilin. The change in drug dissolution on storage involves two competing phenomena of conversion of crystalline drug to amorphous hydrogen bonded state that seems to increase the drug dissolution whereas the phenomenon of Ostwald ripening decreases the drug dissolution. Our studies have shown that Ibuprofen has moderate solubility in both Gelucire and PEG and both the competing mechanisms play moderate roles in determining the solubility of the dispersion granules on storage. Overall this study proposes a formulation technique to increase the solubility and bioavailability of poorly soluble API's that have moderate to good solubility in the dispersion carrier, avoiding the limitations of traditional solid dispersions.

66. Formulation and Characterization of Psycho-Active Drugs Using Various Analytical Techniques

Satya G. Avula, Kenneth S. Alexander and Alan T Riga, Department of Pharmacy Practice, Division of Industrial Pharmacy, The University of Toledo, Toledo, OH

Poor water solubility and slow dissolution into the gastrointestinal tract (GIT) are the two major obstacles impeding the pharmaceutical industry in releasing new dosage forms into the market. These issues have been responsible for the rejection of 70% of the potentially active drugs discovered. The solution to this obstacle is formulating the drugs with known and accepted excipients, which may involve the formation of eutectics. Appropriate mixtures have played a key role in improving the absorption of many compounds by increasing their solubility and dissolution properties. Solving this problem within the pharmaceutical industry will lead to the release of new dosage forms to the market. This study proposes to formulate mixtures of bipolar drugs (e.g. Nortriptyline and Quetiapine fumarate) with excipients (e.g. PEG, Acetyl salicylic acid) and their characterization by various analytical techniques like Differential Scanning Calorimetry, Thermal Gravimetric Analysis, Wide Angle X-Ray Diffraction and Optical microscopy. The blending of the drug with an excipient or a polymer produced a novel product with unique thermal analytical properties and solubility. These new blends, which were prepared, produced compounds which can be used to treat bipolar disorder as well as utilizing the therapeutic properties of the excipients used. Thus, this study proposes a new kind of formulation technique that can increase the dissolution characteristics of poorly soluble drugs while possibly introducing multiple drug therapy.

67. Synthesis and Characterization of Electrorheological Fluids for Medical Devices

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An Electrorheological (ER) process occurs when the viscosity of fluids with dispersed particulates is modified by the application of an electric field. The Electrorheological Fluids (ERFs) studied are dispersions of solid polymers in a low dielectric base oil, typically an insulating fluid. When the ERFs are exposed to a high electric field they demonstrate increased shear stresses, static yield stresses and enhanced viscosity. A mechanism for ER performance is based on the polarization of the dispersed polymer particulates. A critical property of the ER occurrence is the ability of the system to respond to the applied field.

ERFs of recently synthesized Polyaniline.HCl, aged Cellulose fluids, a sample prepared in a Hong Kong lab as well as a commercial ERF from Fludicon® (Germany) were evaluated with a special two probe unit and by Dielectric Analysis (DEA). The polarization or response time is a result of the dielectric evaluation of a fluid in an AC field at an isothermal or scanning temperature mode. The ER response time is directly related to the measured polarization time which is calculated from the critical peak frequency in a Debye plot and is inversely related to the response time. Imaging of the ER event will be demonstrated and the applied voltage and resulting current will be reported.

68. Improved Thermal Mechanical Method for Evaluating Drug Delivery of Tablets and Capsules

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A Thermal Mechanical Analysis (TMA) method has been developed to measure the rate and initial time of drug disintegration. It monitors the physical dimension of the formulated drug as a function of time at 25 or 37°C and pH. The results of this test will meet USP specifications. It measures the expansion, or swelling of the formulated tablet. and monitors the shrinkage or drug disintegration in a fluid. The effect of pH and temperature with time on the rate of delivery was measured. The drugs studied were Femhrt and Aspirin tablets as well as Amoxicillin Capsules. The TMA measures the dimensional stability of the formulated drug as it is immersed in various solutions.

Drug delivery in a specific solution was measured by UV Analysis for the active pharmaceutical ingredient (API). Temperature decreased the disintegration time and increased the rate (mm/min). The amoxicillin 500 mg capsule disintegrated by first absorbing the solvent and softened. The 2nd step was the rounded ends collapsed allowing the drug to be released to the solution. The increased temperature shortened the capsule dissolving time. For the drugs studied pH did not have an appreciable effect on the rate of disintegration. Tablets swell and allow the API to be released others swell and then disintegrate either rapidly over a period of time. This method identified an orally disintegrating drug (at 18 seconds), drug delivered in the stomach, e.g. Femhrt® (< 20 minutes) and the drugs targeted for the intestines (Ritalin® >39 minutes)

69. Determination of the Heat of Solution for Eutectic, Solid Dispersion and Cocrystals of Poorly Soluble Drugs

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Purpose:

The solubility and bioavailability of poorly water soluble drugs can be improved by preparing eutectic, solid dispersion or cocrystals using inert excipients. The purpose of this research was to study solubility behaviour of these compounds with temperature and determine the heat of solution (ΔH_{soln}) from the constructed Van’t Hoffs plots using the experimental equilibrium solubility data.

Methods:

Aspirin, ibuprofen and diflunisal were chosen as model drugs for preparing a eutectic, solid dispersion or cocrystal, respectively. The prepared compounds were analyzed by Differential Scanning Calorimetry (DSC) and Wide Angle X-Ray Diffraction Analysis (XRD) to confirm the structure-property relationship. The solubility at five different temperatures was determined by UV-Visible spectroscopy. The natural logarithm of solubility, in mole fraction, was plotted against inverse of the absolute temperature in order to construct the Van’t Hoffs plot and determine ΔH_{soln} from the slope of the straight line.

Results:

Eutectic, solid dispersion and cocrystal formation was confirmed using DSC and XRD data. The linearity of the van’t Hoffs plots (R^2 of 0.99) indicates that ΔH_{soln} values were constant over the temperature range. All the compounds exhibited a positive ΔH_{soln} (endothermic process) which indicates energy in the form of heat is required to dissolve these compounds in water.

Conclusion:

The experimental data obtained can be a valuable piece of information for the pharmaceutical scientists during preformulation studies. The heat of solution is an important thermodynamic parameter which can characterize physicochemical properties of a eutectic, solid dispersion and cocrystal.

70. Pumice Suspension Stability Utilizing Surfactants

Shikha Rathi, graduate Student and Kenneth Alexander, Industrial Pharmacy, University of Toledo, Toledo, OH

Purpose:
The particle size analysis of drug substances is an important concept for pre-formulation development. In order to make a stable formulation and to improve the sedimentation rate becomes a challenging experience. It is difficult to disperse the particles in a medium without the occurrence of sedimentation. The purpose of this study is to demonstrate how one can retard the sedimentation rate using various surfactants in a mixture of Glycerin & Water as the dispersion medium.
Methods:
It was observed that the size and charge on the surfactants was directly dependent on the molecular weight of the dispersing agent and the charging system. Linear plots were observed using the mono-exponential model equations from Richardson and Zaki, Steinour and Dollimore-McBride theories. The present study involves evaluating various particle sizes of pumice determined by Sieving, Sedimentation, Laser Diffraction Technique and Microscopy. DSC procedures were performed to evaluate the presence of bound water.
Results:
The sedimentation rate for Pumice was slightly reduced when using Tween 20, Benzalkonium chloride and Sodium stearate and it was further reduced by the solvent used.Particles which are retained on each sieve were further examined using microscopy.The particle size obtained was between 44 μ and 53 μ.
Conclusion:
The range of values obtained by sieving was 25-88 mm. Microscopic evaluation of particle shape is a

reliable method to determine the morphology of the particle. A low-temperature DSC procedure was performed to evaluate the presence of bound water.

71. Evaluation of the Volumetric Variation Method to Determine the Powder Porosity and Void Space in Pharmaceutical Dispersions

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Utilizing a beaker and burette, the titration method directly measures the immediate pore volume between the particles rather than determining the solvent taken up in the pores and the coagulation of the particles. The titration method is time-saving, however, no study has shown that it is effective and accurate. The purpose of this study is to evaluate the validity and sensitivity of the titration method in order to determine the porosity of powders. TGA and X-ray Diffraction were used to characterize the powders. Multiple titrations using various powders and pharmaceutical liquid mixtures were performed. Magnesium oxide, glass beads and charcoal were used. Binary mixtures were prepared using Octanol-Ligroine, Methanol-Isopropanol and Glycerin-Water with various compositions. The properties of liquid mixtures including surface tension, viscosity and polarity, and the properties of the powders including particle size were also determined. The results were plotted as weight of solid versus volume of liquid used. The statistical analysis shows the y-intercept is zero for glass beads, but for porous powders the y-intercept was never equal to zero. Non-zero y-intercepts imply that the different solvents, as measured by polarity and dielectric constant, have varying particle-liquid attractive forces. The polarity of the solvent affects the results as well as other parameters of the powders. A mathematic model was established utilizing multiple regression.The results indicate that the titration method is more effective for non-porous powders. For porous powders, the properties of the liquid and powder affect the determination of the porosity of the powders in pharmaceutical dispersions.

72. Structure and Dynamics of Self-Assembling Nanostructures in Isopropyl Myristate (IPM)/Di-Octyl Sodium Sulfosuccinate (DOSS)/Water Ternary Systems

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Purpose: The primary purpose of this study was to study the structure and dynamics of self-assembling nanostructures in Isopropyl myristate (IPM)/di-octyl sodium sulfosuccinate (DOSS)/water ternary systems.
Methods: Ternary mixtures of IPM/DOSS/water were prepared in DOSS-IPM mixtures of various concentrations. The amount of water in the preparations was controlled by modulating the molar concentration of water in each system. The microstructure and dynamics of the formulations were characterized using Photon Correlation Spectroscopy (PCS) in the normal and multi-angle modes. Rheological properties of selected formulations were studied using a controlled stress/strain rheometer. Thermal properties of the ternary mixtures were evaluated via sub-ambient DSC experiments performed from 25ºC to -70ºC.
Results: The ternary systems did not show droplet aggregation or coalescence up to one month as indicated by the multi-angle PCS study. All IPM/DOSS/water systems exhibited Newtonian flow properties. The sub-ambient thermal transitions observed in the ternary systems reported in this study are consistent with the existence of three different types of water. The observed thermal events demonstrate changes in hydration processes that occur at the molecular level as the amount of water in a water-substrate system is systematically increased.
Conclusion: In this study, stable ternary systems were prepared using pharmaceutically acceptable

components. The formulations evaluated in this project have potential for a variety of applications including use as reactors for synthesizing drug nanoparticles.

73. Metal Enhanced Fluorescent Studies of Silver and Gold Nanoparticles

Timothy R. Brewer, Associate Professor, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI and Vamsi Kandimalla, Graduate Student, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI, MI

Studies will be presented on the metal-enhanced fluorescence of tris(2,2'-bipyridyl)ruthenium(II) complex (TBR) in various sizes of silver and gold nanoparticles. The enhancement is due to metal particles concentration the local electric field which increases the intensity of fluorescence in addition to increasing the radiative decay rates. These properties will be investigated using time-resolved fluorescence decay rates in addition to steady-state fluorescence spectra of different metal-TRB systems. Concentration dependence and size of the metal nanoparticle data will be analyzed and interpreted using the theory of metal-enhanced fluorescence in addition to the surface plasmon couple emission theory. In modeling the data, the radiative decay rates and quantum efficiency depend on the proximity of the chromophore to the metal sphere in addition to the dielectric poperties. Thus, the metal nanoparticle type and size should affect these properties. The knowledge of the interaction between molecules and nanoparticles could contribute to the development of sensors for the detection of biomolecular interactions with nanoparticles from weakly emitting species.

74. Photoinduced Electron Transfer Studies in Fullerene Dyads-Tetrads

Jojo Joseph[1], Tuan Nguyen[1], Chien-Lung Wang[2], Stephen Z. D. Cheng[2] and David A. Modarelli[1], (1)Department of Chemistry, The University of Akron, Akron, OH, (2)Goodyear Polymer Center, The University of Akron, Akron, OH

Compounds having electron donor (D) and electron acceptor (A) groups are excellent model compounds to assess electron transfer over long distances. These molecules have potential applications in light-harvesting devices, optoelectronic systems, etc. The aim of this research study involves the photophysical characterization of D-A systems based on covalently bound porphyrin-fullerenes systems with different numbers of C60 fullerenes attached to the porphyrin ring to enhance the electron transfer efficiency. In this poster we report the quantum yield of fluorescence for each molecule, as well as the results of time-resolved fluorescence spectroscopic studies to determine the electron transfer (ET) rate constants, kET.

75. Photochemistry of Hexabromoplatinate and Hexabromoiridate Complexes in Aqueous Media

Igor L. Zheldakov[1], Mikhail N. Ryasantsev[1] and Alexander N. Tarnovsky[2], (1)Chemistry, Bowling Green State University, Bowling Green, OH, (2)Department of Chemistry and The Center for Photochemical Science, Bowling Green State University, Bowling Green, OH

The excited-state and photoaquation dynamics are studied in aqueous $PtBr_6^{2-}$ complex by using ultrafast broadband pump-probe spectroscopy and DFT calculations. The 420-nm excitation to the lowest singlet excited $^1T_{1g}$ state and 530-nm excitation to the lowest triplet excited $^3T_{1g}$ state both lead to the vibrationally hot, coherently excited $PtBr_5^-$ intermediate in its excited triplet state on a 150-fs time scale. This is the first observation of vibrational product coherence in inorganic complexes. Intersystem crossing from triplet to singlet ground-state $PtBr_5^-$ is greatly facilitated by hydrogen bonding, which lowers the corresponding energy gap. The aquated $^1[PtBr_5(H_2O)]^-$ product is formed in about 20 ps after excitation. In addition, novel pump-probe data on photochemistry of the aqueous $Ir(Br)_6^{2-}$ complex will be presented.

76. Experimental and Theoretical Studies of Light-to Heat Conversion in Metal Nanoparticle Solutions

Hugh H. Richardson[1], Michael T. Carlson[1], Peter J. Tandler[2], Pedro Hernandez[3] and Alexander O. Govorov[3], (1)Department of Chemistry and Biochemistry, Ohio University, Athens, OH, (2)Department of Chemistry, Walsh University, North Canton, OH, (3)Department of Physics and Astronomy, Ohio University, Athens, OH

We perform a set of experiments on photo-heating in a water droplet containing gold nanoparticles (NPs). Using photo-calorimetric methods, we determine efficiency of light-to-heat conversion (η) which turns out to be remarkable close to 1, ($0.97< \eta <1.03$). Detailed studies reveal a complex character of heat transfer in an optically-stimulated droplet. The main mechanism of equilibration is due to convectional flow. Theoretical modeling is performed to describe thermal effects at both nano- and millimeter-scales. Theory shows that the collective photo-heating is the main mechanism. For a large concentration of NPs and small laser intensity, an averaged temperature increase (at the millimeter-scale) is significant (~ 7 ^{o}C) whereas, on the nanometer scale, the temperature increase at the surface of a single NP is small (0.02 ^{o}C). In the opposite regime, a small NP concentration and intense laser irradiation, we find an opposite pictures: a temperature increase at the millimeter-scale is small (0.1 ^{o}C) but a local, nanoscale temperature has strong local spikes at the surfaces of NPs (3 ^{o}C). These studies are crucial for the understanding of photo-thermal effects in NPs and for their potential and current applications in nano- and bio- technologies.

77. Ultraviolet-and-532 Nm Laser-Induced Colorless Photoproducts of β-Carotene in Chlorinated Solvents

Aaron E. Beach[1], Wenyue Wang[1], Begum Fouzia[2], Pattraranee Limphong[3], Christie M. Shover[1], Ross E. Jones[3], Jonathan B. McGregor[3], Matthew E. Kelleher[3], Ryan J. Provost[3], Merritt C. Helvenston[4] and Mark B. Masthay[1], (1)Department of Chemistry, University of Dayton, Dayton, OH, (2)Department of Chemistry, Western Kentucky University, Bowling Green, KY, (3)Department of Chemistry, Murray State University, Murray, KY, (4)Department of Natural Sciences, New Mexico Highlands University, Las Vegas, NM

Solutions of the orange plant pigment β-carotene (βC) in carbon tetrachloride (CCl_4) solvent rapidly become colorless upon monophotonic excitation with diffuse, broadband ultraviolet (UV) light or biphotonic excitation with intense green, 532 nm laser pulses. A progressive decrease in the intensity of the λ_{max} = 463 nm absorption band, with a concomitant shift of the absorption maximum toward shorter wavelengths, is suggestive of a progressive decrease in the length of the conjugation pathway via cleavage of the polyene moiety and/or addition across the C=C double bonds. Spectrophotometric characterization of the photoproducts generated in both aerated and deoxygenated CCl_4 solutions is difficult, however, as the final products absorb at wavelengths which lie below the solvent UV cutoff (265 nm). The solvent was accordingly evaporated with a stream of N_2 gas and the photoproducts were subsequently dissolved in n-hexane solvent, which has a much smaller UV cutoff (195 nm). The photoproducts generated in both the presence and absence of oxygen manifest a distinct, narrow absorption band centered at 210 nm. The products generated in deoxygenated solution manifest an additional broad band centered at 310 nm. Gravimetric analysis indicates that the collective mass of the products generated with UV light exceeds that of the parent βC by a factor of 2-4, consistent with the addition of Cl, CCl_3, and oxygen across the double bonds of βC resulting from photoinduced transfer of electrons from βC to CCl_4. A number of potential addition and/or cleavage products containing 2-5 conjugated C=C bonds are proposed.

78. Photochemistry of Nitro-Polycyclic Aromatic Compounds in Solution

R. Aaron Vogt, Christian Reichardt and Carlos E. Crespo-Hernández, Department of Chemistry, Case Western Reserve University, Cleveland, OH

Nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) constitute one of the most troubling classes of environmental pollutants. Concern about these compounds arises partly from their ubiquity: nitro-PAHs are released to the environment directly from a variety of incomplete combustion processes and are also formed in situ by atmospheric reactions of polycyclic aromatic hydrocarbons. However, the larger portion of this concern is rooted in their identification as acutely toxic, mutagenic, and carcinogenic compounds. Photochemical degradation has been proposed to be the main route of natural removal of nitro-aromatic pollutants from the environment. Consequently, studies focused at understanding the photochemistry and the excited state relaxation pathways of nitro-PAHs are essential to predict their fate in the environment.

In this poster presentation, the steady-state and time-resolved photochemistry of several nitro-PAHs in different solvents will be compared. The experimental work is complemented with quantum chemical ground- and excited-state calculations that include solvent effects. It will be shown that the position of the nitro group and its torsion angle relative to the aromatic rings dramatically affects the photochemistry of these compounds in solution. This research was supported by a grant from the American Chemical Society Petroleum Research Fund, Type DNI.

79. Elucidating the Mechanism of Photoisomerization: Ultrafast Studies of the Excited State Properies of Diphenylbutadiene Derivatives

Nicole M. Dickson, Jessica E. Donehue and Terry L. Gustafson, Department of Chemistry, The Ohio State University, Columbus, OH

Photoisomerization plays an important role in biological processes such as the vision process and in molecular switches. 1,4-Diphenyl-1,3-butadiene (DPB) is a linear polyene that exhibits fast decay from its excited state via photoisomerization. We have recently shown that this fast process occurs in <50 ps. Many photoisomerization reactions have been found to occur on the femtosecond time scale. This has lead to the proposal of volume-conserving mechanisms of photoisomerization such as the hula-twist model (HT) and the bicycle-pedal model (BP). We have studied a sterically-hindered derivative of DPB, 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) to attempt to force a volume conserving mechanism of photoisomerization to occur. We have also studied 2,3-diphenyl-1,3-butadiene, a cross-conjugated molecule of the type proposed for use in molecular switches, to elucidate its time constant of photoisomerization.

80. Kinetics and Mechanism of Two Color Reversible Photochromism

Beth Anne McClure and Jeffrey J. Rack, Department of Chemistry and Biochemistry, Ohio University, Athens, OH

Photochromic molecules convert light energy into potential energy which is employed to break certain chemical bonds and form new bonds resulting in a structural change in the molecule. Such molecules have potential use in the development of photoelectrochemical devices and molecular information storage among others. This study has focused on the determination of linkage isomerization in complexes of the type, $[Ru(bpy)_2L]^{n+}$ where L is a bidentate chelating ligand containing a sulfoxide group. By employing femtosecond transient absorption and other spectroscopic techniques, the kinetics and mechanism of isomerization have been determined. Mechanistic attributes of these different systems will be discussed and compared.

81. Ultrafast Transient Absorption Study of a Photoaffinity Labeling Compound - 4-Amino-3-Nitrophenyl Azide

Maxim S. Panov, Mr.[1], Alexander N. Tarnovsky[2], Valentyna Voskresenska[3], R. Marshall Wilson[3], Shubham Vyas[4], Arthur Winter[4] and Christopher M. Hadad[4], (1)Chemistry, Bowling Green State University, Bowling Green, OH, (2)Department of Chemistry and The Center for Photochemical Science, Bowling Green State University, Bowling Green, OH, (3)Department of Chemistry, Bowling

Green State University, Bowling Green, OH, (4)Department of Chemistry, The Ohio State University, Columbus, OH

The photochemistry of the widely used photoaffinity labeling system 4-amino-3-nitrophenyl azide in various solvents has been studied by using ultrafast transient absorption spectroscopy (time resolution, 100 fs). The first singlet excited state S_1 accessed at 420-nm is not photochemically reactive, and predominantly relaxes into vibrationally hot ground state S_0. The 350- and 305-nm excitations to the second singlet excited state S_2 lead to the formation of closed-shell nitrene on a 100-fs time scale followed by its solvent-dependent protonation on 5-20-ps time scales – one of the fastest protonation reactions known to date.

82. Intramolecular Energy and Electron Transfers in Molecular Dyads Comprising of Porphyrin and Ruthenium(II) Bis(2,2':6',2''-terpyridine) Terminal

Shenshen Li and James McCusker, Department of Chemistry, Michigan State University, East Lansing, MI

Molecular Dyads comprising of porphyrin and ruthenium bis(2,2’:6’,2’’-terpyridyl) components have received considerable amount of attention due to their potential applications in artificial photosynthesis and molecular devices. Here we report our progresses towards understanding excited-state behaviors of such dyads, especially the effects of initial excited state localization on the processes of intramolecular energy and electron transfers.

83. Redox Properties of Mercaptoacetic Acid On Gold in Basic Medium

Ewa M. Pater[1], Amanda Aldous[1], Mai Than[1] and Stanley Bruckenstein[2], (1)Department of Chemistry, Plattsburgh State University of New York, Plattsburgh, NY, (2)Department of Chemistry, State University of New York at Buffalo, Buffalo, NY

The behavior of self-assembled monolayers (SAMs) on metal substrates has been extensively characterized from the point of view of their applications, e.g., as sensing and recognizing layers, corrosion preventing layers, or as starting materials for preparation of chemically modified multilayer films. On the other hand, fundamental information related to the adsorption process of SAMs is much more limited. Here we attempt to gain some insight into adsorption process of mercaptoacetic acid (MAA) on polycrystalline gold in basic medium.

Cyclic voltammetry (CV) and open circuit potentiometry (OCP) on a rotating gold disk electrode (RDE) or accompanied by Electrochemical Quartz Crystal Microbalance (EQCM) in 0.5M KOH containing various amounts of MAA (0.0mM to about 7mM) were employed here.

CV reveals an irreversible anodic process of MAA occurring at about +0.35V vs. SCE. The current for this process was studied as a function of MAA concentration and rotation speed (ω). In the presence of MAA the cathodic current corresponding to the reduction of gold oxide decreases; we rationalize this as an inhibition of the surface oxidation of gold in basic medium by MAA.

In OCP experiments, the reaction between dissolved MAA and the oxidized gold surface produces a potential transient. The transient time decreases exponentially with increased concentration of MAA but it is not affected by ω.

The RDE and EQCM data strongly suggest that both chemical and electrochemical processes are involved in the interaction between MAA and gold in 0.5M KOH.

84. Residual Gas Analysis During Thermal Control Surface Testing In the Lunar Dust Adhesion Bell Jar

James R. Gaier, NASA-GRC, Cleveland, OH

The effectiveness of thermal control surfaces during the Apollo program was compromised when they became even partially covered with lunar dust. These dust effects are being simulated in the

Lunar Dust Adhesion Bell Jar in an attempt to understand the relationship between sub-monolayer dust coverage and thermal performance. Future studies will assess the effectiveness of mitigation strategies. Processes in the simulation include baking the lunar simulant under vacuum to greater than 200°C, and exposing it to both air plasma and hydrogen-helium plasma. Both the dust and the samples, AZ-93 paint and Ag/FEP, were exposed to heating with a xenon arc lamp as well. Thus, the system contains multiple sources for out-gassing. The partial pressures of ten residual gases were monitored using a quadrupole mass spectrometer during more than 50 tests. This paper describes the results of the analysis of the residual gas composition, which provides a window into the processes taking place.

85. Permeation Sampling of Gasoline In Water

Cody Allen Anderson and James Hardy, Department of Chemistry, The University of Akron, Akron, OH

The EPA reports nearly 110,000 underground gasoline storage tank leaks in the United States. The EPA methods for detecting these leaks in groundwater currently requires liquid-liquid extraction and purge-and-trap methods which are both time consuming. A method has been developed using passive sampling and thermal desorption for a solventless determination of gasoline components in groundwater. The major components of interest were benzene, toluene, ethyl benzene, and the three isomers of xylene (BTEX). A silicon polycarbonate membrane was adhered to a glass tube and the membrane was exposed to a water sample. Inside the tube an adsorbent, Tenax TA, was placed to collect the components passing through the membrane. The Tenax TA was then placed in the thermal desorption unit for injection and analysis in a GC-FID. Time-weighted average (TWA) curves were created relating amount of analyte collected to the product of concentration and exposure time of each of the BTEX components. There was found to be a linear relationship on all TWA plots. This method has the advantage of employing continuous monitoring rather than the grab sampling used in the EPA methods.

86. Development of a Packing Material for the Clean-up of Samples From Environmental Sources by GPC

Thomas Dent, Graham Cleaver, Greg Saunders, Ben MacCreath and Graham Margetts, Polymer Characterization, Varian, Inc., Walnut Creek, CA

Monitoring trace levels of small molecules such as pesticides in plant and animal matter has become a routine requirement in many environmental analysis laboratories. Techniques such as GC/MS are employed to measure levels of trace pollutants. These methods first require removal of the bulk organic matrix such as the lipids and oils.

Gel permeation chromatography (GPC) is an ideal technique for cleaning up environmental samples prior to further analysis. Separating molecules on the basis of size in solution, GPC can be used to remove relatively large, high molecular weight fats and lipids from smaller low molecular weight pesticides and other species of interest. The separation is easily performed using simple equipment and common organic solvents. Typically, so-called ‘soft gel' materials are employed; low cost, gravity-packed microporous beads that are swollen in solvent prior to packing, to introduce the pore structure. Unfortunately, such materials are typically not robust and prone to packing issues, and care must be taken to produce optimum results.

Varian, Inc. has developed a new material for use in environmental sample clean-up applications. Based on microporous particles of co-polymerized styrene and divinyl benzene, the new material is robust enough to be supplied dry in-column for `in situ` swelling and packing without the need for a separate ‘column packing' step. This greatly enhances the ease of use of the material without compromising performance. This poster discusses the new material and illustrates the performance in sample clean up applications.

87. His-HDX Method to Probe the Microenvironment of Histidine Residues in Escherichia Coli Dihydrofolate Reductase

Masaru Miyagi, Case Center for Proteomics and Bioinformatics, Case Western Reserve University, Cleveland, OH and Chris Dealwis, Department of Pharmacology, Case Western Reserve University, Cleveland, OH

We recently developed a mass spectrometric method for probing the microenvironment of indivisual histidine residues in proteins (Analytical Chemistry, 80, 6481-6487, 2008). The method is referred to as "Histidine Hydrogen-Deuterium Exchange Mass Spectrometry (His-HDX-MS)", because the method measures the rate constant (k_φ) of pH-dependent hydrogen-deuterium (H-D) exchange at the imidazole C_2-proton of histidine residue using mass spectrometry. His-HDX-MS provides two useful parameters: pKa and the half-life ($t_{1/2}$) of H-D exchange reaction. The former indicates the electrostatic environment and the latter indicates the solvent accessibilities of individual histidine residues.

His-HDX-MS was applied to probe ligand-induced changes of the microenvironment of five histidine residues in dihydrofolate reductase (DHFR), which plays a central role in maintenance of cellular pools of 5,6,7,8-tetrahydrofolate. Free DHFR, DHFR in complex with folate and $NADP^+$, and DHFR in complex with methotrexate (MTX) and NADPH were incubated in D_2O with different pD at 37 °C for 72 hr. After the incubation the protein was digested by proteases and the resulting peptides were analyzed by LC-MS/MS. The pKa and $t_{1/2}$ values for the five histidine residues in free DHFR, DHFR-folate-$NADP^+$ and DHFR-MTX-NADPH were successfully determined from the sigmoidal plots of k_φ against pD. The results will be discussed using the X-ray crystallography data available for the DHFR structures.

88. Development of An HPLC-MS/MS Test Procedure to Quantify 4-Ketocyclophosphamide,Cyclophosphamide and Ifosfamide In Human Urine

Clayton B'Hymer, Division of Applied Research and Technology (DART), National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH

An accurate and precise test procedure was developed to detect and quantify the level of 4-ketocyclophosphamide (4-keto-CP), cyclophosphamide (CP) and ifosfamide (IF) in human urine. 4-Keto-CP is a metabolite and possible biomarker for exposure to CP, an anticancer drug and health concern for exposed healthcare workers. IF is another commonly used anticancer drug also of concern for healthcare worker exposure. Urine sample preparation for this test procedure consisted of liquid-liquid extraction (LLE) of the target analytes from urine with ethyl acetate. Quantification was by means of a high-performance liquid chromatography (HPLC) with tandem mass spectrometric (MS/MS) detection. A deuterated analog of CP was used as a procedural internal standard for this test procedure. Accuracy and precision of this test procedure was demonstrated by means of recovery experiments. Recovery varied between 97 and 105% of spiked levels for the three target analytes with relative standard deviations of 8.4% or less. The limits of detection (LOD) were determined to be approximately 1 ng/mL for 4-keto-CP, 0.1 ng/mL for CP and 0.05 ng/mL for IF in urine. These data, other figures of merit and factors of the development and validation of this test procedure will be described.

Disclaimers: Mention of company names and/or products does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH). The findings and conclusions in this abstract have not been formally disseminated by NIOSH and should not be construed to represent any agency determination or policy.

89. In-Situ Desalting and Derivatization in Reactive Desorption Electrospary Ionization (DESI) for the Detection of Monosaccharides

Yun Zhang[1], Caroline Krieger[1], Dina R. Justes[2], Feng Feng[1] and Hao Chen[1], (1)Department of Chemistry and Biochemistry, Ohio University, Athens, OH, (2)Department of Chemistry, Purdue University, West Lafayette, IN

We have reported previously a method for rapid detection of sugars via `in-situ` derivatization with phenylboronic acid $PhB(OH)_2$ using reactive desorption electrospray ionization (DESI, `Chem. Commun.` 2006, 597). The present study describes an improved method that employs modified phenylboronic acids including 3-nitrophenylboronic acid and `N`-methyl-4-pyridineboronic acid iodide. In contrast to using $PhB(OH)_2$, enhanced sensitivity of using 3-nitrophenylboronic acid was observed due to the stabilization of the resulting boronate ester anion by its electron-withdrawing nitro group and the limit of detections (LODs) for glucose in water using 3-nitrophenylbornic acid and phenylboronic acid were determined to be 0.1mM and 0.5 mM, respectively. In the case of `N`-methyl-4-pyridineboronic acid iodide, the corresponding LOD is 5μM and the higher sensitivity obtained is attributed to the efficient ionization of both the reactive DESI reagent and product since the precursor acid with a quaternary ammonium group is pre-charged. In this case, two additional important features are found: i) unlike using $PhB(OH)_2$, the experiment, performed in the positive ion mode, is applicable to neutral and acidic saccharide solutions, facilitating the analysis of biological fluids without the need to adjust pH; ii) simply by changing the spray solvent from water to acetonitrile, the method can be used for direct urine glucose analysis via `in-situ` desalting, due to the low solubility of urine salts in the sprayed organic solvent. The method reported in this study with improved sensitivity along with its high selectivity could find significant applications in saccharide analysis in complicated biological samples.

90. What Is σ-Hole Bonding?

Monica C. Concha[1], Pat Lane[1], Jane S. Murray[2] and Peter Politzer[2], (1)Department of Chemistry, University of New Orleans, New Orleans, LA, (2)Department of Chemistry, Cleveland State University, Cleveland, OH

σ-Hole bonding is a noncovalent electrostatically-driven interaction between a covalently-bonded atom of Group IV - VII and a negative site. Its basis is a region of positive electrostatic potential on the outer portion of the Group IV - VII atom, arising from a deficiency of electronic charge in the outer, noninvolved lobe of the orbital involved in the covalent bonding; this deficiency is known as a σ-hole. σ-Hole bonding is highly directional, along the extension of the covalent bond to the Group IV - VII atom. Its strength increases with the polarizability of the Group IV - VII atom, and the electron-withdrawing power of the remainder of the molecule; it is often competitive with hydrogen bonding. Examples will be given of the importance of σ-hole bonding in molecular biology and in materials science.

91. A Fluorescence Laboratory Utilzing Spectral Subtraction to Study Ligand Binding

Stephanie Bilinovich, Department of Chemistry, Akron University, Akron, OH and Peter J. Tandler, Department of Chemistry, Walsh University, North Canton, OH

A laboratory exercise has been developed to study the binding of Eosin Y to BSA. This experiment is a multi-week exercise that attempts to simulate a research environment where spectral overlap of the free and bound species occurs. Eosin Y is a red dye with green fluorescence that undergoes a 9 nm chromatic shift when bound to BSA. The fluorescence emission spectra are collected from samples that contain a constant Eosin Y concentration and varying amounts of BSA. The sample set contains two limiting cases: one when no BSA is present so that a pure Eosin Y fluorescence emission spectrum can be collected and a second when the concentration is so high that essentially all the Eosin Y is bound to BSA so that a pure bound Eosin Y spectrum can be obtained. As the

concentration of the BSA increases a spectral shift occurs as more of the Eosin Y is bound to BSA. A spectral subtraction method is used to determine the amount of free and bound Eosin Y. Once the free and bound concentrations of Eosin Y are determined a Scatchard type analysis is performed.

92. Designing Metal-Organic Framework Structures Utilizing A Combination of N- and O- Donor Ligands

Scott D. Bunge and **Kristin A. Gore**, Department of Chemistry, Kent State University, Kent, OH

At Kent State University, in the Spring 2008 semester, the REEL module modeled scientific research by allowing approximately thirty General Chemistry II students to design, synthesize and characterize novel metal-organic framework structures. Over a three week period, students were given a choice of six different N- and O- donor ligands and a choice of metal precursors. Prior to the synthesis, students consulted with a research advisor in an effort to outline their individual procedure. A research project was agreed upon and a synthetic investigation was undertaken. From the individual experiments performed, crystals were isolated and analyzed using a single crystal X-ray diffractometer. Further analysis of the novel compounds was done using UV-VIS, FT-IR, NMR, and Elemental Analysis.

93. Kinetic and Mechanistic Studies of the Deuterium Exchange in Classical Keto-Enol Tautomeric Equilibrium Reactions

Michael A. Nichols and Mark J. Waner, Department of Chemistry, John Carroll University, Cleveland, OH

An extension of the classic keto-enol tautomerization of β-dicarbonyls into a kinetic analysis of deuterium exchange is presented. It is shown that acetylacetone and ethyl acetoacetate undergo substantial deuteration of the β-carbon in the presence of methanol-d_4. The extent of deuteration may be monitored via NMR spectroscopy. A mechanism for deuteration is presented and shown to be consistent with a consecutive first order process. The data for acetylacetone are consistent with steady state kinetics, while those of ethyl acetoacetate illustrate non-steady state behavior, offering an accessible example where students might collect and analyze real data to examine the applicability of the steady state approximation.

94. Cosmetic, Forensic and Environmental Science Workshops for K-12 Students

Larry Kolopajlo, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI

The areas of cosmetic, forensic and environmental science (CFES) are both relevant and interesting to children of all ages. The purpose of this paper is to describe CFES workshops that have been successfully conducted by university chemistry faculty for the benefit of visiting high school students and teachers. The workshops have been designed to encourage both diverse underrepresented groups to take an interest in chemistry.

95. Summer Enrichment Programs to Increase Diversity in STEM Fields

Sarah S. Preston and Jeanette Nappier, Department of Chemistry and Physics, Ursuline College, Pepper Pike, OH

Currently the workforce in the STEM fields does not reflect the diversity of this country as a whole, thereby missing the opportunity to gain strength from a diverse perspective. Often, students from under-represented groups have less exposure to science and scientific career opportunities and therefore pass up educational opportunities in high school to prepare for these careers. Summer Science Saturdays encourages rising sophomores and juniors to consider a science-based career by highlighting educational opportunities, providing role models, and introducing science-based career options. Science FIRST allows rising seniors to strengthen their scientific backgrounds while viewing science through the lens of current global problems. These two programs are strategically linked to provide continuing support for students with an appreciation for science.

96. Review of Recent Total Syntheses of Nonracemic Natural Products That Include Key Photocycloaddition Steps

Wendell L. Dilling, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI

This poster reviews several recent publications where photocycloaddition reactions of nonracemic unsaturated compounds served as key steps in the total syntheses of natural products. The photocycloaddition reactions involved the following types of compounds that resulted in nonracemic cycloadducts: an alpha, beta-unsaturated gamma-lactone, a 5-alkylidene-2(5H)-furanone, an omega-pentenyl-1,3-cyclohexadiene, a quinolone, and an omega-pentenylbenzene. The final nonracemic natural products prepared by the synthetic sequences were (−)-merrilactone A (Inoue, et al), (+)-tetracyclic core of bielschowskysin (Sulikowski, et al), (−)-biyouyanagin A (Nicolaou, et al), (+)-meloscine (Bach, et al), and (−)-penifulvin A (Gaich, Mulzer).

97. ACS Presidents From the Midland Section

Wendell L. Dilling, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI

Two men from the Midland (Michigan) Section have been elected to the American Chemical Society presidency. Dr. Edgar C. Britton served as president in 1952, and Dr. Thomas H. Lane is serving in 2009. At the time of his election, Britton was director of the organic research laboratory and vice chairman of the executive research committee at The Dow Chemical Company in Midland. Lane is director, global science and technology outreach, and a research scientist at Dow Corning Corporation in Midland, a subsidiary of The Dow Chemical Company and Corning Incorporated. Both men received part of their college education in Indiana and Michigan. Britton studied at Wabash College and received B.A. and Ph.D. degrees from the University of Michigan. Lane received B.S. and M.S. degrees from Purdue University and Central Michigan University, respectively. Britton's emphases during his presidential year were expanding original research in order to lay the foundation for future chemical businesses, establishing a balance between original and developmental research, maintaining and expanding ACS publications and Chemical Abstracts, and utilizing military reservists to support a large active military and an industrial and agricultural program for the US. Lane's emphases during his presidential year are keeping education and science literacy at the forefront of our thinking and pivotal in our actions, keeping an open mind, hearing all voices, and practicing tolerance and acceptance as ACS continues to reach out, building new and productive relationships that support the ACS strategic plan, and developing outcome-based metrics to guide ACS.

98. Neutron Scattering in Chemistry

Cora Lind, Department of Chemistry, University of Toledo, Toledo, OH

Oak Ridge National Laboratory is home to two of the world's most powerful neutron sources: the High Flux Isotope Reactor and the Spallation Neutron Source. These facilities are designed and operated to assist users in using neutron scattering to probe the structure and dynamics of materials. This poster gives an overview of opportunities that can help chemists in their research through the use of neutron scattering techniques.

99. Structure and Electrochemical Behaviour in Lithium-Ion Batteries of LiFePO4OH and Its Proton Ion-Exchanged Derivative FePO4.H2O

Laurence Croguennec[1], Nicolas Marx[1], Dany Carlier[1], Alain Wattiaux[1], Lydie Bourgeois[2], Pierre Kubiak[1], Frédéric Le Cras[3] and Claude Delmas[1], (1)Icmcb - Cnrs, University of Bordeaux, Pessac, France, (2)Ism, University of Bordeaux, Talence, France, (3)Drt/Liten/Dtn/Lce, CEA, Grenoble, France

Since the very interesting properties, especially in terms of thermal stability, discovered for $LiFePO_4$ as positive electrode in lithium-ion batteries, a lot of groups focuss their researches on the study of polyanionic materials as possibly new alternative electrodes for lithium-ion batteries. Here we will report the synthesis of a new phase $FePO_4.H_2O$, obtained from tavorite $LiFePO_4(OH)$ through a Li^+/H^+ exchange and isostructural to already reported $VPO_4.H_2O$ and $MnPO_4.H_2O$. The ion-exchange reaction was shown to be topotactic, indeed the structures of $LiFePO_4OH$ and $HFePO_4OH$ (or $FePO_4.H_2O$) are very similar and both characterized by chains of FeO_6 octahedra, interconnected through PO_4 tetrahedra, such as the resulting framework encloses different types of tunnels. A neutron diffraction study has allowed the localization of lithium and hydrogen in these two stuctures, revealing that the hydrogen atoms are linked to the oxygen atoms shared by two adjacent FeO_6 octahedra and that the lithium atoms are present in five oxygen coordinated sites. The nature of the -OH and $-OH_2$ groups in $LiFePO_4OH$ and $FePO_4.H_2O$ respectively was confirmed by vibrational spectroscopies, whereas the difference in number and nature of iron sites was well characterized by Mössbauer spectroscopy. Lithium intercalation was shown to occur in these two phases through the reduction of Fe^{3+} to Fe^{2+}, at an average voltage of ~2.5V vs. Li^+/Li for $LiFePO_4OH$ and of ~2.8V for $FePO_4.H_2O$. Good cyclability was obtained for the two systems.

100. MnO2/C COMPOSITES as POSITIVE ELECTRODE MATERIALS for RECHARGEABLE ELECTROCHEMICAL CELLS

Thoa T.P. Nguyen and Trung Q. Pham, Department of Chemistry (University of Science), Vietnam National University - Hochiminh City (VNU-HCM), Ho Chi Minh, Vietnam

Manganese dioxide has been considered as a promising candidate for positive electrode materials of rechargeable cells because of the natural abundance and environmental compatibility. Several effective methods have been developed to improve the characteristics of the manganese dioxide/carbon composite (MnO_2/C) electrode which had been used conventionally as cathode for primary cells. In the present work, composites composed of manganese dioxide (MnO_2) and various mesoporous carbon powders were anodically co-deposited onto a graphite substrate by the electrolyze of the manganese acetate $Mn(CH_3COO)_2$ solutions containing carbon black, carbon paste, carbon nanotube, nanoliquid carbon and carbon slurry with various particle size. The surface morphology and crystal structure of the electrodes have been examined by Scanning electron microscope (SEM), Transmission electron microscope (TEM) and X–ray diffraction (XRD) techniques. Cyclic voltammetry (CV) has been applied to evaluate the electrochemical capacitance performance of the prepared electrodes. The highest capacitance values were obtained for composite electrodes prepared with anodic current density of 0.25 to 0.35 mA/cm^2 and total charge of 1.5 to 2.0 C/cm^2. Mesoporous carbon additives increased the capacitance and improved the electrochemical properties of the manganese dioxide electrode. Optimized samples exhibit specific capacitance values of around 200 - 250 F/g in the range of 0-1.0 V vs. SCE with excellent cyclability in 2 M KCl electrolyte.

101. Characteristics of Spinel Lithium Manganese Oxide Synthesized From Chemical Manganese Dioxide as Positive Electrode Materials for Lithium Ion Cells

Binh T. X. Lam, Thoa T.P. Nguyen and Phung M.L. Le, Department of Chemistry, UNIVERSITY OF SCIENCE, VNU-HCM, Ho Chi Minh City, Vietnam

Lithium manganese oxide ($LiMn_2O_4$) spinel compound were synthesized by melting impregnation method using manganese dioxide (MnO_2) and lithium nitrate. The raw materials MnO_2 were prepared by oxidation of manganese sulfate ($MnSO_4$) with potassium persulphate ($K_2S_2O_8$). Synthesized MnO_2 contained mostly body-centered pyrolusite and tetragonal pyrolusite b-MnO_2. The SEM images showed that spinel $LiMn_2O_4$ obtained in spherical particles with diameters from 0.5 µm to 1 µm. The XRD pattern of the synthesized $LiMn_2O_4$ showed that the product did not contain Mn_2O_3 impurities; and its lattice parameter was smaller than that of the standard $LiMn_2O_4$ spinel. The charge-discharge cycling behavior in Swagelok model of lithium-ion cells, using synthesized $LiMn_2O_4$ as cathode, lithium metal as anode and $LiPF_6$ as electrolyte with Whatman glass separator, showed that the product has high capacity value (³ 90 mA.h/g) and low capacity fading rate during continuous charge-discharge cycling.

Keywords: chemical MnO_2, spinel $LiMn_2O_4$, melting impregnation, lithium-ion cell.

102. Characterization and Application of Electrochemical Environmental Biosensors

Marcela Ovalle and Margarita Stoytcheva, Instituto de Ingenieria, Universidad Autonoma de Baja California, Mexicali, Mexico

This work proposes a new approach for detection and quantification of environmental contaminants (pesticides, heavy metals and fluorides), based on the application of electrochemical bacterial and enzyme sensors. The performances of three types of electrochemical biosensors employing respectively acetylcholinesterase, Arthrobacter Globiformis and Leptospirillum Ferrooxidans as biological recognition element, were investigated. The values of the enzyme reaction kinetic parameters: I_{max}, K_M^{app}, and K_I were established under kinetically controlled conditions for various pH and temperature values. The analytical characteristics of the determinations were evaluated according to IUPAC recommendations. It was demonstrated that such sensors could represent a simple, rapid and economic alternative to standards methods applied for organophosphorus pesticides, heavy metals and fluorides quantification.

103. Effect of Electrolyte Additives and Cell Treatment On the Open-Circuit Voltage of the Dye-Sensitized Solar Cell

Thoa T.P. Nguyen, Hoang T. Nguyen and Hai M. Tran, Department of Chemistry, UNIVERSITY OF SCIENCE, VNU-HCM, Ho Chi Minh City, Vietnam

The nanocrystalline dye sensitized solar cell has attracted a great interest as a low cost alternative to solid-state junction devices for the conversion of solar energy into electricity. In this paper the performance of dye-sensitized solar cells (DSC) based on nanocrystalline titanium dioxides with N719 as sensitizer was investigated as a function of 4-tert-butylpyridine (TBP) and guanidine thiocyanate (GuSCN) addition to the I^-/I_3^- redox electrolyte. The open-circuit voltage (V_{OC}) was increased from 0.56 V to 0.78 V by addition of GuSCN (0.20 M) and TBP (0.5 M).
The cathode potential was increased from 0.09 V to 0.18 V (versus Ag/AgCl electrode) by addition of 0.1 and 0.5 M of GuSCN respectively. TBP (0.5 M) addition increased the cathode equilibrium potential by 35 mV and V_{OC} by 130 mV.

High V_{OC} values of the DSC cells were obtained using TBP treatment in which, before filling the cell with the electrolyte, pure TBP (5 µL) was injected into the cell and kept for some seconds, subsequently the excess TBP was removed by a vacuum pump. After the first TBP treatment cycle, a V_{oc} = 0.86 V was obtained using an optimized electrolyte mixture (LiI/I_2 ratio = 0.15 M/0.05 M, TBAI 0.15 M (or PMII 0.6 M), TBP and GuSCN additive concentrations 0.5 M and 0.2 M respectively). After two TBP treatment cycles a maximum V_{OC} = 0.90 V was obtained compared to V_{oc} = 0.80 V for a cell which was not treated by the TBP injection technique.

Solid State Chemistry (1)

Organizer: Cora Lind University of Toledo, Toledo, OH
Organizer: Catherine M. Oertel Oberlin College, Oberlin, OH
Presider: Catherine M. Oertel Oberlin College, Oberlin, OH

Session Overview: Solid-state chemistry is aimed at the synthesis and characterization of advanced materials. Understanding materials' properties based on the structure of materials, and fine-tuning properties through the study of structure-property relationships, ties together diverse areas like nanomaterials, semiconductors, crystal growth and engineering. In this symposium, new materials, synthetic routes and characterization methods will be presented.

104. Site Occupation and Electrical Properties of Manganese-Doped $CuInSe_2$

Jennifer A. Aitken[1], Jin-Lei Yao[1], Pierre Ferdinand Poudeu Poudeu[2] and Nathan J. Takas[2], (1)Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA, (2)Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, LA

$CuInSe_2$-based materials are a viable alternative to silicon for use in photovoltaic devices. $CuInSe_2$ adopts the chalcopyrite structure, which can be derived from the cubic, sphalerite structure by doubling the unit cell in one direction such that the crystal system becomes tetragonal. In the structure there are two crystallographically unique cation sites, namely 4a and 4b. In this study, two series of compounds, $CuIn_{1-x}Mn_xSe_2$ and $Cu_{1-y}In_{1-y}Mn_{2y}Se_2$, were prepared via high-temperature, solid-state synthesis. Single-phase materials could be found up to x=0.10 and 2y=20%, respectively. The bandgap of the materials, estimated from optical diffuse reflectance spectroscopy, remains at approximately 0.9 eV independent of doping concentration. Rietveld refinement of neutron powder diffraction data revealed that the Mn ions have a site preference, independent of the nominal composition. Thermopower and electrical conductivity data will also be presented.

105. Synthetic Pyrite (FeS_2) and Its Characterization

George L. Schimek, Ph.D., Energizer Battery Manufacturing, Inc., Westlake, OH

Naturally occurring pyrite, FeS_2, is the active cathode material in Energizer's Ultimate and Advanced Lithium AA and AAA products. Laboratory-prepared pyrite is currently being synthesized and characterized. This presentation will discuss a relatively low temperature synthetic route to pyrite using iron oxide, sulfur and hydrogen sulfide. The resulting sub-micron material has been characterized by X-ray diffraction, electron microscopy, elemental analyses, surface area, as well as thermal response and electrochemical behavior. These results will be highlighted against the challenges of oxidation that exist when working in an iron sulfide system.

106. Polychalcogenide Flux Synthesis, Structure and Characterization of Quaternary, Lithium-Containing Diamond-Like Semiconductors

Meghann A. Moreau, Jonathan W. Lekse, Jin-Lei Yao and Jennifer A. Aitken, Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA

Diamond-like semiconductors (DLS) are normal valence compounds that adopt the cubic or hexagonal diamond structures. DLS are of interest due to their potential uses in nonlinear optics, solar cells and spin-based electronics. Quaternary DLS, such as I_2-II-IV-VI_4, have been less studied. Due to the compositional flexibility of these quaternary compounds, chemical substitutions can be made allowing the fine-tuning of the materials' physical properties. Two new phases have been prepared in this work, Li_2CdSnS_4 and Li_2MnSnS_4. Li_2CdSnS_4 has been prepared as orange, needle-like single crystals from a lithium polysulfide flux at 650°C. The flux proportions are crucial since small changes in the parameters lead to the formation of unwanted impurities. Li_2CdSnS_4 is water and air stable. The compound crystallizes in the noncentrosymmetric, orthorhombic space group $Pmn2_1$ with unit cell parameters of a = 7.9555(3), b = 6.9684(3) and c = 6.4886(3) angstroms. Final R indices of the single crystal refinement were R1 = 0.0247 and wR2 = 0.1081 for all data. In this structure, the lithium, cadmium and tin cations are tetrahedrally coordinated by sulfur to form a three-dimensional distorted honey-comb network. If the Li-S bonds are considered to be more ionic than covalent, the structure can be considered as $[CdSnS_4]^{-2}$ layers sandwiched between lithium cations. The band gap of Li_2CdSnS_4 was determined to be 3.1 eV. Additionally, the materials have been characterized with diffuse reflectance UV-VIS-NIR spectroscopy, powder X-ray diffraction, single crystal X-ray diffraction, differential thermal analysis (DTA) and second harmonic generation (SHG) testing.

107. Synthesis of Colloidal Ag Nanocrystals and Their 2D Superlattices

Ravi Shankar and **Terry P. Bigioni**, Department of Chemistry, University of Toledo, Toledo, OH

Ligand-passivated colloidal nanoparticles are novel building-block materials whose physical and chemical properties can be designed independently. Nobel metal nanoparticles are particularly interesting for their dramatic optical properties, including the absorption of light and the transfer of that energy. While gold nanoparticles are easy to use, silver has superior optical properties due to the lack of single electron transitions in the visible part of the spectrum. The chemistry of silver nanoparticles is more complex than that of gold, however, their synthesis is non-trivial. We have developed a synthetic route for making small thiol-passivated silver nanoparticles under aerobic conditions, and where core and shell are synthesized separately. After dodecanethiol ligand addition, elemental analysis by EDS and XPS shows thiol derivatization. Large-angle XRD and HRTEM confirms the presence of a metallic Ag core with a diameter of 5.6±0.4 nm. A competitive by-product of this reaction is large platelet-shaped crystals of silver thiolates, which can be controlled with reaction conditions. Small-angle XRD shows up to 28 orders of reflections for these crystals, with d-spacings that depend on the thiol chain length. Monolayers of silver nanoparticles have been prepared by drop drying, similar to previous work on gold nanoparticles. Formation of 3D superlattices were also observed by concentrating the nanoparticle solution beyond the saturation concentration, analogous to crystallization of sugar or salt from a supersaturated solution. The use of Au and Ag monolayers as plasmonic sensors was also investigated.

108. Synthesis, Characterization and Reactivity of Alumina Nanofibers

Anna M. Pischera, John O'Brien and Matthew P. Espe, Department of Chemistry, The University of Akron, Akron, OH

We have developed methods for producing alumina (Al_2O_3) nanofibers with sub-micron diameters, high aspect ratios, and in different phases using electrospinning methods. These nanofibers are being investigated for application in absorption and decomposition of toxic phosphonate compounds, including chemical warfare agents (CWAs). The bulk and surface composition and structure of these materials are being studied by solid-state NMR as a function of the synthetic process (electrospinning and calcination). Application of ^{27}Al NMR has allowed the determination of the distribution of 4, 5 and 6 coordinate aluminum sites within the nanofibers. By using surface selective NMR methods, the distribution of these aluminum coordination sites on the surface is observed to differ from those in the bulk and to be highly sensitive to calcination temperature. The alumina nanofibers have been reacted with the CWA stimulants methyl phosphate ($MePO_4$) and dimethyl methyl phosphonate (DMMP). ^{31}P and ^{13}C NMR characterization has detected both physisorbed and chemisorbed phosph(on)ate species, and the ratio of these species is highly dependent on the nanofiber surface structure. The products of the hydrolysis reaction between the alumina surface and phosph(on)ates have been identified and will be discussed. In addition, the reaction of the alumina nanofibers and $MePO_4$ resulted in the dissolution of surface alumina.

109. Controlling Materials Structure with Surface Chemistry

Simon Garcia, Department of Chemistry, Kenyon College, Gambier, OH

The shape and arrangement of crystals within a material can affect its overall physical and chemical properties, but the rational control of crystal shape is a challenge, especially in photovoltaic materials like zinc oxide, titanium dioxide, and silicon. Solution-phase crystal growth and etching reactions offer an attractive means of controlling crystal shape in these materials, because these reactions can be directed by shape-control ligands: organic molecules that bind to crystal surfaces. To explore this approach in zinc oxide crystallization, the effects of multidentate ligands on the shape of zinc oxide crystals were compared. The aspect ratio (length / width) of hexagonally prismatic crystals is correlated with ligand denticity (number of binding sites). A monocarboxylate ligand (glycolate) has no effect on crystal shape, while dicarboxylate (malate) and tricarboxylate (citrate) ligands reduce the aspect ratio, resulting in flat, disk-like crystals. This effect is dependent on ligand concentration. Crystal aspect ratio is correlated with crystal length, but not with width. These trends suggest that multiple binding sites enable ligands to bind specifically to the hexagonal face of zinc oxide and to inhibit deposition on this face. The number of binding sites is not the only factor, however; the effects of related carboxylate ligands suggest that binding site type and configuration mediate the effect of denticity. These ligands can be used in the growth of zinc oxide films to control their nanoscale structure.

110. Crystal Engineering of Metal-Organic Frameworks

Sibrina Collins[1], Roland Falcon[1], James Aryeetey[1], William B. Connick[2], J. A. Krause[2] and Stephen Taylor[2], (1)Department of Chemistry, College of Wooster, Wooster, OH, (2)Department of Chemistry, University of Cincinnati, Cincinnati, OH

Metal-organic frameworks (MOFs) remain a popular area of interest for potential applications of fuel storage. Four metal salts, $FeCl_2.6H_20$, $MnCl_2.4H_20$, $CoCl_2.6H_2O$ and $La(CF_3SO_3)_3.xH_20$ were reacted with p-phenylenebis(picolinaldimine (pbp) at room temperature using crystal engineering technology. X-ray analysis reveals that $[FeCl_2(pbp)].2CH_3OH$ (**I**) is a 1-dimensional (1-D) coordination polymer. Little interaction between the parallel zigzag chains is observed, the separation distance is 8.2 Å. As a result, a relatively open framework is adopted with cavity sizes suitable for small guest molecule (e.g. methanol) incorporation. Intermolecular interactions with the methanol stabilize the open framework.

Analytical Chemistry (1)

Sponsor: Analytical Division of ACS
Organizer: Rebecca Whelan Oberlin College, Oberlin, OH
Organizer: John F. Turner Cleveland State University, Cleveland, OH
Presider: Rebecca Whelan Oberlin College, Oberlin, OH

Session Overview: These sessions feature advances in measurement science broadly understood, including instrumentation development and application to problems of environmental, biomedical, and industrial relevance.

111. Polymerized Crystalline Colloidal Array Photonic Crystals for Chemical Sensing and Optoelectronics

Sanford A. Asher, Ph.D., Department of Chemistry, University of Pittsburgh, Pittsburgh, PA

We have developed a novel class of smart optical materials based on soft materials which are responsive to their environment and which can be actuated chemically or photonically. Highly charged, monodisperse colloidal particles will self assemble in water into crystalline colloidal arrays (CCA), which are either body centered or face centered cubic structures. We have developed smart materials from these self-assembled structures, which utilize the highly efficient Bragg diffraction of light from the CCA periodicity. We polymerized these CCA into acrylamide hydrogels. These CCA-embedded hydrogels show the rich volume phase transition phenomena characteristic of these soft materials. These materials act as frequency agile optical filters. We have functionalized these hydrogels with dyes and photochromic molecules, as well as with molecular recognition agents which cause the hydrogel to change volume in response to either photons, or the presence of specific analytes (eg Pb^{2+}, glucose etc). The resulting volume changes alter the array spacing, which causes the diffracted light wavelength to shift, or causes the diffraction efficiency to change. We will discuss the volume phase transition properties of these arrays and also describe the use of these arrays as chemical sensors, novel ns optical switching materials, and optical memory devices.

112. Combining Visible Spectroscopy with Atomic Force Microscopy to Correlate the Optical Properties of Au Nanoplatelets with Antibody\Antigen Binding

Srinivas reddy Beeram and Zamborini Francis P, Department of Chemistry, University of Louisville, Louisville, KY

Gold nanoparticles have interesting optical properties which can be used for applications in biosensing. We synthesized ~200 nm wide Au nanoplatelets on silicon by a seed-mediated growth method and used them for human IgG detection after immobilizing anti humanIgG on the Au nanoplatelets through covalent linking. We used UV-vis spectroscopy to monitor the optical changes during antibody/antigen coupling to Au nanoplatelets and Atomic Force Microscopy (AFM) to image the antibody and antigen on the surface of the nanoplatelets. We controlled the location of antibodies on the edges of the platelets by performing a thiol place exchange reaction between mercaptoundecanoic acid and mercaptoethanol functionalized platelets before coupling the antibodies to the acid groups via EDC and NHS activation. Under certain conditions, we immobilized individual antibody on the platelet surface and imaged them with AFM before and after IgG binding. UV-VIS spectra showed that the surface Plasmon band of the Au nanostructures changes more significantly for antibody/antigen coupling on the place-exchanged surfaces. These studies show that the sensitivity of the optical properties of Au nanostructures depends on the location of the biological receptor. This is an important finding for optimizing these materials for biosensing applications. Future experiments will correlate the number and position of antibody/antigen on the surface with the optical properties by combining AFM imaging and Rayleigh scattering at the single particle level. We want to determine the optimal detection limit of these protein sensors, which is of importance in disease diagnostics and biological studies.

113. Gradient Elution in Microchannel Electrochromatography

Jared M. Mudrik, Michael W.L. Watson and Aaron R. Wheeler, PhD, Department of Chemistry, University of Toronto, Toronto, ON, Canada

There is great interest in using microfluidic channels packed with a stationary phase for chemical separations of complex mixtures. A key advantage of such techniques is the use of electroosmotic flow (EOF), controlled simply by applying electrical potentials between reservoirs. A disadvantage for this technique, however, is a lack of compatibility with gradient elution separations. This limitation arises from the dependence of EOF velocity on run buffer content (including the concentration of organic modifier). We introduce a method for implementing gradient elution in electrochromatography in which multiple run buffers are velocity-matched, such that the elution profile resembles that found in conventional HPLC. This method is driven entirely with EOF, meaning that pumps, valves and pressure fittings are not required. The method was validated by application to separations of peptide standards and protein digests. These results suggest that microfluidic electrochromatography may be compatible with a wide range of applications that have previously been unexplored.

114. Folding-Based Electrochemical DNA Sensor: Alternative Sensor Substrate and Probe Immobilization Strategy

Rebecca Y. Lai, Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE

Here we report a folding-based electrochemical DNA (E-DNA) sensor fabricated on a gold-plated screen-printed carbon electrode. We show that the E-DNA sensor is not required to be fabricated on a relatively flat gold surface; the sensor works comparably well when fabricated on an electrodeposited gold film with a surface roughness factor of ~7. This study demonstrates the feasibility of using an inexpensive electrode substrate for disposable sensor fabrication. Another advance in the E-DNA sensing technology is the adaptation of Sharpless "click" chemistry in the fabrication of the sensor. The "click" chemistry-based E-DNA sensor shows essentially identical sensor sensitivity, selectivity, response time and regenerability when compared to results obtained from a sensor constructed via the conventional "two-step" method while offering unprecedented sensor fabrication versatility. The combined technology will be an important advancement towards realization of cost-effective multi-element biosensor arrays for field applications.

115. Novel Approach to the Characterization of Pharmaceutical Excipients Reveals New Dielectric Visco-Elastic Properties by Thermal Analytical Methods

Alan Riga, PhD[1], K.S. Alexander, PhD[2] and Hareesha Reddy Venumuddala, BSPS[1], (1)Department of Chemistry, Cleveland State University, Cleveland, OH, (2)Pharmacy Practice, The University of Toledo, Toledo, OH

Millions of dollars are expended on pharmaceutical testing to qualify excipients for fully formulated drugs, medicines, and active ingredients. Individual and interactive properties of excipients and drugs are needed to predict their action in the human body. Dielectric Analysis [DEA] and Differential Scanning Calorimetry [DSC] methods were employed to screen the most widely used drug excipients seeking new properties to assist pre-formulation studies. The following excipients were examined by DEA: calcium phosphate, cotton seed oil, croscarmellose, gelatin, mannitol, peanut oil, polyethylene glycol, pioneer sugar, plasdone, sodium alginate, sodium lauryl sulfate, sodium starch glycolate, sodium stearate, a sorbitol solution, canola oil, anhydrous lactose, and benzoic acid. A comparison of DSC and DEA thermal curves based on the same excipient indicates that major endothermic events, e.g. volatilization or melting, are also delineated by fundamental DEA properties, with an exponential rise in permittivity and dielectric loss factor (conductivity). The focus of this research was to study the DEA electrical conductivity, permittivity and tan delta vs. frequency as a function of temperature. The premelt DEA properties varied significantly leading to new dielectric visco-elastic properties. Crystalline excipients have a low electrical conductivity (ca.10^{-1}pS/cm) while their amorphous form has an exceptionally high electrical conductivity (ca.10^{7} pS/cm). Relative amorphous and crystalline content of the excipients can be determined by DEA. There is an extraordinary event in the solid state prior to melting which can be associated with the creation of excited molecules, excimers. This revelation can lead to new synthesis and reaction paths.

116. Fundamental Studies of Reaction and Collision Cell Processes in ICP-MS

Patrick J. Gray, Dept. of Chemistry and School of Earth Sciences, The Ohio State University, Columbus, OH, John W. Olesik, School of Earth Sciences, The Ohio State University, Columbus, OH and Susan V. Olesik, Dept. of Chemistry, The Ohio State University, Columbus, OH

Inductively coupled plasma mass spectroscopy provides elemental and isotopic selectivity and sub part per trillion detection limits for elements with an abundant isotope that does not suffer from spectral overlaps. Spectral overlaps can result from isobaric, multi-charged or polyatomic ions generated from argon, the solvent or the sample matrix. Chemical resolution can be used to decrease spectral overlap ion signals by several orders of magnitude through ion molecule reactions. Collision induced dissociation and kinetic energy discrimination are typically less efficient but can also reduce molecular ion signals.
Ion-molecule reactions that may be useful for ICP-MS will be assessed using experimental data coupled with theoretical modeling. Thermodynamics predict whether or not a reaction will proceed. However, kinetics determine how effective a reaction gas will be to remove signals due to undesired ions. The appropriate model for reaction cross section (hard sphere, Langevin, ADO) depends on the kinetic energy of the ions. Ions enter the reaction cell with approximately 8 eV kinetic energy but become thermalized after a few collisions, altering the effective collision cross section. The

importance of spin selection rules for electron transfer reactions, which may prohibit certain reactions from occurring, will be examined. The efficacies of ion-molecule reactions, collision induced dissociation, and kinetic energy discrimination to overcome spectral overlaps in ICP-MS will be compared.

117. Semi-Quantitative Elemental Analysis Using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in the Presence and Absence of High Ca Concentrations

Josh R. Dettman[1], John W. Olesik[2] and Susan V. Olesik[1], (1)Deptartment of Chemistry, The Ohio State University, Columbus, OH, (2)School of Earth Sciences, The Ohio State University, Columbus, OH

Using semi-quantitative analysis the concentrations of the 69 elements measurable by ICP-OES could be determined based on a standard containing just one element of known concentration. This requires that a measured plasma temperature accurately predicts the relative sensitivities of all emission lines used. The local thermodynamic equilibrium (LTE) model relates temperature to relative sensitivity assuming that collisional decay with electrons is the only de-excitation mechanism. However, experimentally measured LTE temperatures depend on the element and emission line used for the measurement. LTE based relative sensitivities may err by up to a factor of 100.

A correction to the LTE model can be made by accounting for radiative decay. Using the resulting partial-LTE (pLTE) model, plasma temperature can be determined from an ion to atom emission intensity ratio. Sensitivities of all emission lines can be estimated relative to one or more lines in a standard based on the measured temperature and the pLTE model. The relative sensitivities can then be used to determine the approximate concentrations of all elements in the sample. Because changes in plasma temperature due do the sample matrix are measured for the standard and samples, this method should be less sensitive to plasma matrix effects than external calibration.

In this presentation the incorporation of radiative decay into the LTE model will be discussed. Temperatures determined from different elements using the pLTE model will be compared. The accuracy of concentration results in samples with low concentrations of dissolved solids and with high concentrations of Ca will be presented.

Computational Chemistry (2)

Organizer: Jane S. Murray Cleveland State University, Fairview Park, OH
Organizer: Peter Politzer Cleveland State University, Fairview Park, OH
Presider: Peter Politzer Cleveland State University, Fairview Park, OH
Presider: Jane S. Murray Cleveland State University, Fairview Park, OH

Session Overview: Acknowledgements: We greatly appreciate the support provided by the U. S. Office of Naval Research and the Computers in Chemistry Division of the American Chemical Society.

118. Computational Design of New Enzyme Activities

Tore Brinck, Professor, Physical Chemistry, Royal Institute of Technology (KTH), Stockholm, Sweden

The last decades of research in biocatalysis has demonstrated that enzymes often can use alternate catalytic mechanisms and catalyze more than one chemical transformation. This catalytic promiscuity, which is inherent to many biocatalysts, may be utilized in the redesign of enzymes to obtain new catalytic activities. We have found the catalytic machinery of serine hydrolases particularly useful for the transformation of carbonyl compounds. Using a combination of quantum chemical calculations and molecular dynamic simulations, we have shown that mutating a single residue, the catalytic serine, in Candida antarctica lipase B (CALB) results in an enzyme that can catalyze a number of reactions important in organic synthesis, including aldol addition, Michael type additions and epoxidation. In addition, the mutant shows no activity for the natural reaction of CALB, i.e. ester hydrolysis. In this lecture we will review the computational methodology for analyzing catalytic activity towards unnatural reactions in wild type and mutant enzymes. The latest progress towards catalysis of reactions involving carbon-carbon bond formation in lipases will be reported. The studied reactions include different types of nucleophilic additions as well as Diels-Alder.

119. Computational Approach to Interactions of Anti-Cancer Metallodrugs

Jaroslav V. Burda, Dep. of Chemical Physics, Charles University, Prague, Czech Republic

Cisplatin (diammine-dichloro-platinum(II) complex) and its derivatives are known for their high activity in the anticancer treatment. The physico-chemical background of the activation of these drugs in the hydration process of replacing chloro-ligards by water molecules was examined. Thermodynamic and kinetic parameters were determined for this hydration reaction. Comparing with experimental data it can be seen very good agreement of both characteristics. The process of cisplatin activation can be understand purely on the thermodynamic footings as formation of less stable Pt-complexes under the LeChatelier-Braun-van Hoff's principle of chemical equilibrium. On this basis hydration rate and cytotoxicity index were compared for several platinum complexes.

Also some other transition metals were explored. Detachment of the chloro-ligand in $[\text{ruthenium(II)(arene)(en)Cl}]^+$ was studied and compared with cisplatin activation. Thermodynamic potentials and rate constants for activation and interactions with purine nucleobases bases were estimated. Comparison with measured data demonstrates a power of such computational tools for further investigations.

120. Molecular Dynamics Simulations and Signal Transduction

Timothy Clark, Computer-Chemie-Centrum, Universitaet Erlangen-Nuernberg, Erlangen, Germany

Signal transduction is the process by which biological processes or events are controlled. The controlling agent may be a small molecule, a peptide or a modification of the protein such as phosporylation. Until very recently, we believed that signal transduction occurred on time scales too long for molecular-dynamics (MD) simulations. However, our recent work has shown that signal-transduction movements of the tetracycline repressor protein (TetR) can be observed in MD simulations of 50-100 nanoseconds. TetR is the archetypical signal-transduction system that is responsible for the main mechanism of resistance of Gram-negative bacteria to the tetracycline class of antibiotics. However, its use as a "gene switch" in both eukaryotes and prokaryotes allows genes to be turned on and off at will by administering a tetracycline.
We have been able to determine the mechanism of induction of TetR by tetracyclines at the atomic level using 50 nanosecond MD simulations and to explain the "reverse phenotype", mutant TetR variants that display the reverse behavior to the wild type (i.e. they are induced in the absence of tetracyclines and not in their presence).

Subsequent simulations have demonstrated that we can identify induction reliably using simple geometric criteria, but only if the simulations are long enough as allosteric rearrangements often first occur after 50 or more nanoseconds. The implications of these simulations for the mechanism of induction (especially with respect to the proposed pre-equilibrium mechanism) will be discussed.

121. Interactions of Metal Clusters with DNA Bases

Jerzy R. Leszczynski, Department of Chemistry, Jackson State University, Jackson, MS

This talk highlights the most significant achievements and challenges related to our recent studies on interactions of DNA fragments with nanomaterials. Among studied species are fullerenes, carbon nanotubes, metal and metal oxide clusters. Application of computational techniques allows obtaining detailed information on changes of the DNA fragment properties interacting with fullerene and metal clusters.

Energy Storage and Energy Conversion: Electrocatalysis (2)

Sponsor: CH Instruments; Cincinnati Student Chapter, ECS
Organizer: Shouzhong Zou Miami University, Oxford, OH
Organizer: Yuriy Tolmachev, Dr. Kent State University, Kent, OH
Presider: Yuriy Tolmachev, Dr. Kent State University, Kent, OH
Presider: Shouzhong Zou Miami University, Oxford, OH

122. Pt COVERAGE DEPENDENT ELECTROCATALYTIC ACTIVITIES in Ru@Pt and Au@Pt CORE-SHELL NANOPARTICLES

YuYe Tong, Associate Professor, Chemistry, Georgetown University, Washington, DC

It this presentation, we report a comparative investigation of the coverage dependent electrocatalytical properties of Ru@Pt and Au@Pt core-shell nanoparticles (NPs). For Ru@Pt NPs, controlled Pt adlayers of mono-atomic height were deposited on commercial Ru NPs using a one-pot ethylene glyco based method and were characterized by TEM, XRD, and electrochemical CO stripping voltammetry. Samples with 11 different Pt coverage values ranging from 5% to 93% were prepared and investigated. The steady-state MeOH electro-oxidation current density of the Ru@Pt NPs measured by chronoamperometry showed a volcano curve, with the peak appearing at the coverage of 31%. The optimal peak activity was ~150% higher than that of the industrial benchmark PtRu (1:1) alloy NPs. Fundamentally, such a volcano curve in reaction current is the result of the two competing processes of the MeOH electro-oxidation: the triple dehydrogenation of MeOH that prefers more Pt ensemble sites and the elimination of poisonous CO that is enhanced by more adjacent Ru/Pt sites via the so-called bifunctional mechanism and also by possible electronic effect at the low Pt coverages. For Au@Pt NPs, controlled Pt adlayers with 10 different coverages varying from 40% to 300% were deposited onto homogenously distributed Au NPs of two different sizes, i.e., 6.5 nm and 17.5 nm respectively. Electrochemical data point to a much stronger Au-Pt interaction as compared to Ru-Pt interaction, which leads to characteristically different electrocatalytic behaviors. Stronger metal-adsorbate interaction renders Au@Pt NPs less active for both MeOH electro-oxidation and ORR.

123. Self-Assembled Core-Shell Nanoporous Metals for Oxygen Reduction

Jonah Erlebacher, Materials Science and Engineering, Johns Hopkins University, Baltimore, MD

We discuss recent advances in the use of dealloyed metals for electrocatalysis in fuel cell reactions, where dealloying refers to the selective electrochemical dissolution of one component from a homogeneous multi-component alloy under conditions where the remaining components reform into a highly porous metal, typically with pore and ligament sizes < 10 nm. Porosity results from a kinetic competition between dissolution rates and surface diffusion rates. This competition can lead to control of pore size, but also to control of surface composition. We show in particular that the addition of small amounts (< 5%) of Pt to base alloys (Ag/Au, Pd/Ni) stabilize the resultant porosity to thermal annealing and oxidation/reduction potential cycling, leading to enhanced morphological stability. The reason for this is a self-organized segregation of Pt to pore surfaces, essentially creating self-assembled (Pt shell)-(core) mesoporous metals, akin to core/shell nanoparticles, but with intrinsic good electrical contact to all points on the surface. We will also present results on the oxygen reduction activity of these Pt-skin mesoporous metals. Finally, fabrication of these alloys into ultra-thin foils 100 nm thick possess extremely low loadings of Pt and other precious metals, and we will discuss their integration into actual hydrogen/oxygen fuel cells.

124. Recent Advantages in Pt Monolayer Fuel Cell Electrocatalysts

Kotaro Sasaki, Jia Wang, Miomir Vukmirovic, WeiPing Zhou and Radoslav Adzic, Chemistry Department, Brookhaven National Laboratory, Upton, NY

Over the last several years we inaugurated a new class of electrocatalysts for the ORR based on a monolayer of Pt deposited on metal or alloy carbon-supported nanoparticles. The Pt-mass activity of several of these electrocatalysts was several times higher than that of commercial Pt/C samples. Long-term fuel cell tests demonstrated their good stability. The origin of their high activity was identified by electrochemical and surface-science techniques, x-ray absorption spectroscopy (XAS), and density functional theory calculations. These catalysts have the potential to alleviate the principal drawbacks in cathode electrocatalysts for the ORR, including, its slow kinetics, high Pt loadings, and poor long-term stability.

Their properties (activity, stability) depend `inter alia` on the degree of order of the structure of the Pt monolayer. To synthesize Pt monolayers as almost ideal shells on carbon-supported Pd nanoparticles we have employed a modified method of galvanic displacement of underpotentially (UPD) deposited Cu monolayer. We also developed in depositing in a Cu-mediated layer-by-layer growth of Pt onto carbon-supported Pd nanoparticles close to ideal monolayer-to-multilayer Pt deposit. Atomic structures of these electrocatalysts have been studied by `in situ` XAS and STEM/EELS. Recent results demonstrated that a Pd interlayer to fin-tune a Pt_{ML}-core interaction may improve the activity. The results with Pt monolayer electrocatalysts may significantly impact science of electrocatalysis and fuel-cell technology, as they have demonstrated an exceptionally effective way of using Pt that can resolve problems of other approaches, including electrocatalysts' inadequate activity and high Pt content.

125. Ionic Liquids Adsorption and Desorption Dynamics During Gold Electrode Oxidation and Reduction Processes

Yu Du and Xiangqun Zeng, Department of Chemistry, Oakland University, Rochester, MI

Room temperature ionic liquids (RTILs) have received great interests in electrochemical applications due to their unique properties such as good conductivity, wide potential window, excellent thermal stability and zero vapor pressure, etc. The nature of interface and interaction between the electrode and electrolytes is an important topic in electrochemistry which play central role in the electrochemical kinetic process. Only in these few years, there are a few reports on study of interfacial properties of ILs on electrode surfaces; however little work about the in situ surface information of the electrodes during the electrode oxidation and reduction process in RTILs has been reported. In this work, three of the RTILs were studied, they are [C6mpy][Tf2N], [MeBu3N][Tf2N], and [bmim][Tf2N]. Electrochemical quartz crystal microbalance (EQCM) was employed to investigate the in situ adsorption/desorption of electrolytes on gold electrode during the non-faradic and faradic process in ionic liquids solvent, which was realized by in situ monitoring the mass change at the surface of electrodes. In the faradic region, obvious absorption/desorption of the cation of IL on the gold electrode were observed. Beside the potential applied, the adsorption/desorption properties of IL on the gold electrode are also dependent on the structure of the cations of IL, and a steric hindrance effect between the cation of IL and electrode was suggested to responsible to the facts. In addition, the absorption/desorption of electrolytes were obviously effect the properties of the electrical double layer on the electrodes.

126. The Durability of Pt and Pt Alloys as Fuel Cell Cathode Catalysts

Ting He, Honda Research Institute USA, Columbus, OH

The direct conversion of chemical energy to electricity via fuel cells has attracted significant attention for many decades. However, due to the sluggish kinetics of oxygen electroreduction and particularly the poor durability of fuel cell system in service, the mass utilization of fuel cells has been inhibited. To overcome the technical barriers associated with fuel cell durability, it is necessary to understand the degradation mechanisms of oxygen reduction electrode and propose countermeasures.

In this presentation, I will report our new findings on the mechanisms of coarsening and corrosion of Pt and Pt alloys under oxygen reduction conditions: the coarsening processes were monitored by in-situ electrochemical scanning tunneling microscopy (EC-STM), and the corrosions were measured using inductively coupled plasma – optical emission spectroscopy (ICP-OES). It has been found that the coarsening is caused by potentiostating under double-layer potentials whereas the corrosion is resulted from RedOx processes of potential cycling.

In addition to these in-situ analyses, the proposed degradation mechanisms were verified by testing Pt catalysts under real fuel cell operating conditions. The fuel cell testing results are in consistent with the model proposed. Details of these new findings will be discussed and countermeasures will be proposed.

127. Third Generation of PEFC Catalytic Layers

Yuriy Tolmachev, Dr. and R. Hoover, Dept. of Chemistry, Kent State University, Kent, OH

Pt load reduction remains an important goal for cost reduction and sustainability of automotive PEFC technology. We will present a new design of carbon-free PEFC catalytic layers based on non-noble metal nanowires coated with monolayer thick Pt shell. Modeling calculations suggest that such layers can generate 14 kW of power from 1 g of Pt. The use of Atomic Layer Deposition for Pt coating and the activity of the resulting core-shell catalyst in ORR will be discussed.

128. Catalytic Reduction of Weak Acids by [CoCp(η^4-C_8H_{12})] Isomers

William E. Geiger[1], **Michael J. Shaw**[2] and James E. Eilers[2], (1)Department of Chemistry, University of Vermont, Burlington, VT, (2)Department of Chemistry, Southern Illinois University - Edwardsville, Edwardsville, IL

Protonation of the 19-electron [CoCp(η^4-1,5-COD)]$^-$ anion (**1**$^-$) leads to a 17-electron [CoCp(η^3-C_8H_{13})] complex (**2**). Complex **2** also forms upon reduction and protonation of the cyclooctene-diyl complex [CoCp(η^3,η^1-C_8H_{12})] (**3**). The formation of **2** is the first step in a catalytic series of reduction / protonation reactions which appear to involve a rare cobalt η^3-cyclooctenyl hydride intermediate, and electron-transfer induced η^3 to η^1- isomerization. Chemical reductions, simulations of CV results, DFT calculations, bulk electrolysis results, and magnetic resonance data are presented.

129. High Performance of Nano-Structured PtRuRh Ternary Catalysts towards Ethanol Electrooxidation

Jayati Datta and Susmita Singh, Department of Chemistry, Bengal Engg Sci University, Shibpur, Howrah, India

This work reports an improved electro–catalytic activity of PtRhRu nanoparticles towards ethanol oxidation in acid medium for direct ethanol fuel cells, compared to binary or single Pt catalyst. The carbon supported multi-metallic catalysts at different compositions were synthesized through the borohydride reduction method and were characterized in terms of their relative electrochemical activity employing techniques like cyclic voltammetry, polarization study, chronoamperometry and electrochemical impedance spectroscopy. Compositional and structural characterizations of the catalyst layers were carried out through EDX, TEM and XRD analysis. All of these catalysts consisted of uniform nano-sized particles of narrow size distribution with the average particle size being always less than 5.0 nm. The shift in the X–ray diffraction peaks with incorporation of Ru and Rh in the Pt crystal structure was indicative of the extent of alloying among the catalyst constituents.

A negative shift in the onset potential and high ethanol oxidation current density was observed on the PtRhRu catalyst compared to the other catalysts. The charge transfer resistance, as obtained from impedance spectra, was significantly reduced at the RhRu modified Pt electrode surface, reflecting an increase in reaction kinetics of the electro-oxidation process. The reaction product analysis, during the course of ethanol electro-oxidation shows that the presence of Rh accelerates the C-C bond scission and promotes the electro-oxidation towards completion. With higher catalytic property than Pt and the binary alloys, this ternary Pt-RhRu electro-catalyst could be a promising candidate for fuel cell applications.

Forensic Science (2)

Sponsor: Thermo Scientific
Organizer: Douglas Rohde Lake County Crime Laboratory, Painesville, OH
Organizer: John Goodpaster Indiana University Purdue University Indianapolis (IUPUI), Indianapolis, IN
Organizer: Frank Miller Cuyahoga County Coroner's Office, Cleveland, OH
Presider: Douglas Rohde Lake County Crime Laboratory, Painesville, OH

Session Overview: The Forensic Science Symposium will offer participants an overview of prevalent chemical principles, methods, instrumentation and research involved in the analysis of physical evidence and their application to the legal system.

130. Phencyclidine in Driving Impairment in Lake County, Ohio

Douglas E. Rohde, M.S. and Amanda J. Jenkins, Ph.D., Lake County Crime Laboratory, Painesville, OH

The authors present the case history and toxicological findings of several impaired driver cases in a one-year period (June 2007 - June 2008) that revealed the presence of phencyclidine. Phencyclidine (PCP) is a dissociative drug with hallucinogenic and neurotoxic properties. Initially introduced as a surgical anesthetic post WWII, it was subsequently discontinued due to the preponderance of adverse psychoactive effects. PCP works as an N-methyl-D-Aspartate (NMDA) receptor antagonist; blocks dopamine reuptake and elevates synaptic dopamine levels. PCP has been shown to produce hallucinations, disorientation, image distortion, mood disorders, memory loss and paranoia. As a recreational drug, PCP is commonly ingested by smoking plant material (marijuana, herbs) dipped in or sprayed with the liquid form. Other routes of administration include insufflation, intravenous injection, oral ingestion and potential transdermal absorption. Toxicology testing was performed on all cases, using ELISA for initial drug screening and GC-NPD and GC-MS for confirmation and quantitation. PCP blood concentrations ranged from 40 to 90 ng/ml. NHTSA reports blood PCP concentrations ranging from 10 to 180 ng/mL (mean 73 ng/mL) in 50 subjects arrested for driving under the influence of PCP. Prior to 2007 there were only two impaired driver cases in a five-year period (2002 - 2006) that were reported as positive for PCP in Lake County, OH.

131. Optimization of a Microwave-Assisted Extraction (MAE) Procedure for the Extraction of Organic Impurities From Seized MDMA Tablets

Patricia J. Joiner, B.S., Forensic Science Program, School of Criminal Justice, Michigan State University, East Lansing, MI and Ruth Waddell Smith, Ph.D., Department of Chemistry, Michigan State University, Forensic Science Program, School of Criminal Justice, Michigan State University, East Lansing, MI

The potential of microwave-assisted extraction (MAE) followed by headspace solid-phase microextraction (HS-SPME) for organic impurity extraction from seized 3,4-methylenedioxymethamphetamine (MDMA) tablets was investigated. MAE allows for highly efficient extractions while HS-SPME allows for the selective extraction of impurities. This research focused on the MAE optimization using a HS-SPME procedure that was previously developed in our laboratory.

A simulated MDMA tablet was used for the optimization of the MAE procedure. The sample was dissolved in an aqueous buffer, microwave extracted, and subsequently extracted using HS-SPME. A factorial experimental design was used to screen for the important parameters in the MAE and to evaluate the interaction of the different parameters. Parameters investigated included extraction time, extraction temperature, and heating rate. A central composite design was then used to optimize the most important parameters determined by the factorial design. The optimized MAE procedure was subsequently compared to conventional LLE procedures for the extraction of organic impurities from seized MDMA tablets.

132. The ABC 's of BZP and TFMPP in Northeast Ohio

Szabolcs Sofalvi[1], Eric S. Lavins[1], Paul D. Boggs[2] and Douglas E. Rohde[2], (1)The Office of the Cuyahoga County Coroner, Cleveland, OH, (2)Lake County Crime Laboratory, Painesville, OH

`Objective:` The aim of this study was to assess the presence of 1-benzylpiperazine (BZP) in solid-dose and biological samples and to determine the potential of abuse by two separate demographic groups: postmortem samples obtained during autopsy and human performance specimens from law enforcement agencies. BZP belongs to a group of aryl-substituted piperazines that includes among others `m`–CPP and TFMPP. They have become widely popularized as party drugs worldwide. In many countries, these drugs are abused as legal recreational alternatives to methamphetamine and MDMA. BZP is a chemically synthesized CNS stimulant and is predominantly a synthetic sympathomimetic. It can stimulate and inhibit reuptake of dopamine and serotonin, the two neurotransmitters responsible for the psychoactive properties. It has no current pharmaceutical use and was classified as a Schedule I controlled substance in the United States in 2002.

Methods: The blood and urine specimens were subjected to a three-step liquid-liquid extraction procedure. The extracts were assayed underivatized on an HP 6890 GC interfaced with an HP 5973 MSD in full scan mode using a DB-5ms capillary column. A five-point calibration curve 10 mg/L with pheniramine as the internal standard and a positive control at 5 mg/L was utilized.

`Conclusions:` The presence of BZP and TFMPP in clandestine tablet submissions and postmortem samples has increased notably in Northeast Ohio in recent months and should be monitored for future trends in regards to abuse potential and toxicological concerns in postmortem specimens.

133. Automated Raman Correlation within a Mineral Database

Nikolas J. Neric, B.S. and John F. Turner II, Department of Chemistry, Cleveland State University, Cleveland, OH

Raman spectroscopy is an analytical method that is beneficial for mineral studies because it is nondestructive, chemically specific, and requires little or no sample preparation. However, creating a database that is open to contribution from other Raman investigators is difficult due to the variety of instruments used to collect data. We have recently developed a new spectral matching algorithm that suppresses instrument dependent artifacts. Our approach diminishes the effects of baseline shifts and offsets, non-sample dependent band shifts, and variations in the Raman band intensities that result from different sample orientations relative to the laser polarization axis or different excitation wavelengths. The result is set of correlation scores that describe the chemical similarity of an unknown sample to every spectrum in the database. We present our current efforts to incorporate our new algorithm into our library of Raman data in an effort to create a fully automated system which will be open to contribution from any Raman investigator.

134. The Future of Forensic Science Education in Light of the National Academy of Sciences (NAS) Report 2009

Dennis J. De Luca, Ph.D., Department of Biological and Allied Health Sciences, Ohio Northern University, Ada, OH

The February 2009 Report of the National Academy of Sciences (NAS) entitled "`Strengthening Forensic Science in the United States: A Path Forward`" outlined necessary changes for the training, research and education in the forensic sciences. Particular to all in the forensic community are Recommendation 10 of the Executive Summary and Chapter 8 of the Report proper. These sections outline three purposes of Education and Training: 1) "to prepare the next generation of forensic practitioners", 2) "to formalize and require continuing education of forensic scientists and" 3) "to educate judges, lawyers and law students". The Report indicates that prospects for employment are excellent. The Report, also, mandates for the requirements of many undergraduate and graduate programs in forensic science programs to be enhanced and therefore be the keystone to improved education and research in the field of forensic science. The American Academy of Forensic Sciences through its Forensic Science Educational Program Accreditation Commission already has as its mission to provide a seal of quality to an educational institution. To summarize and recommend the Report states "To attract students…in multidisciplinary fields critical to forensic science practice, Congress should authorize and appropriate funds to the National Institute of Forensic Science (NIFS) to work with...graduate educational institutions"…placing "emphasis on developing and improving research methodologies applicable to forensic science". Whereas these recommendations will necessitate an enormous investment the recommendations are those by which forensic science is to be validated not just a practice but as a true scientific discipline through support for education and research.

135. Cleveland's Most Remembered Murder Mystery - the Sheppard Case

Elizabeth K. Balraj, M.D., Cuyahoga County Coroner's Office, Cleveland, OH

On the fourth of July, nineteen fifty four, Marilyn Reese Sheppard, a thirty one year old white female was found dead in her Bay Village home. Her husband, who was a prominent physician in the Community, was the one who found her body. Their only son, age 5, was in the home when this incident took place.

Autopsy showed that she died as a result of multiple blunt impacts to head and face. Her death was ruled homicide by assault by Dr. Samuel R. Gerber, then Coroner of Cuyahoga County. Autopsy also revealed that Marilyn Sheppard was pregnant. Extensive investigation by the law enforcement officials and the Coroner lead to the arrest of her physician husband.

Dr. Sheppard however denied any wrong doing and claimed that a bushy haired stranger committed the crime. During the second trial he was found, "not guilty. For the third trial techniques and tests which were not available in the fifties were used to investigate this death. The results of these modern techniques along with all of the investigation of this case was presented to the jury at the third trial.

Today's presentation will give an overview of the Sheppard Case as it evolved from nineteen fifty four to its final chapter and conclusion during the third trial. Many books have been written and movies have been filmed based on this tragic incident. Yet the desire on the part of the general public to hear more about the Sheppard case has not waned.

Functional Materials: Multi-Functional Polymeric Materials (1)

Organizer: Gary E. Wnek Case Western Reserve University, Cleveland, OH

136. Organosilica Supersorbents That Instantly and Reversibly Swell: Opening New Frontiers In Environmental Remediation, Actuator-Based Chemical Sensing, and Water Purification

Paul L. Edmiston, Associate Professor of Chemistry, Department of Chemistry, College of Wooster, Wooster, OH

Swellable organically modified silica (SOMS) is a sol-gel derived hybrid organic-inorganic material that instantly swells 8-times its dried volume upon exposure to non-polar chemical species either as neat liquids or dissolved in water or air. The material is extremely hydrophobic and does not swell in water. SOMS have been demonstrated to absorb butanol, acetone, BTEX, and chlorinated solvents from water with broader specificity and higher capacity than activated carbon. Swelling is completely reversible by vaporizing the absorbed organic material allowing for simple regeneration and recovery of adsorbed contaminants. The swelling process is generates forces in excess of 100N/g as the matrix expands. The highly tensioned glass matrix will swell in the presence of propane, butane, and toluene vapors. Numerous applications of SOMS have been demonstrated. Currently, SOMS-based materials have gone from bench-scale testing to production-scale testing and are being employed in the clean-up dissolved organic contaminants at EPA sites in Ohio. Other uses of SOMS will be described including actuator-based chemical sensing, drug delivery, drinking water purification, and natural gas purification.

137. Stimuli-Responsive Optoelectronic Liquid Crystal/Polymer Composite Fibers and Films

Ebru A. Buyuktanir[1], Margaret W. Frey[2] and John L. West[1], (1)Liquid Crystal Institute, Kent State University, Kent, OH, (2)Fiber Science and Apparel Design, Cornell University, Ithaca, NY

The development of ultrafine stimuli responsive LC/polymer composite fibers is presented. These photonic fibers are comprised of a low molecular weight liquid crystal (LC) incorporated into polymeric fibers via two approaches: electrospun LC/polymer fibers and photopolymerized substrate-free polymer dispersed LC (PDLC) films and fibers. In the former method, the composite LC fibers consisting of 4-pentyl-4′ -cyanobiphenyl (5CB) and polylactic acid (PLA) are collected onto a copper plate as a nonwoven mat, as well as onto a diamond shape aluminum collector, in order to obtain uniformly aligned fibers. In the latter method, substrate-free PDLC films and fibers are produced by using a polymerization-induced phase separation method. We investigate the formation, morphology, LC optical texture, and alignment of the LC fibers. In the electrospinning method, this is achieved by experimenting with process parameters, such as applied voltage, collection distance, and flow rate of the polymer solution. The morphology and optical properties of composite LC/polymer fibers are studied with scanning electron microscopy (SEM) and polarizing optical microscopy (POM), respectively. Phase transition characteristics of the composite LC/polymer fibers are also studied to evaluate mesophase characteristics of LC materials within the core of the fibers. Most importantly, it is observed that the LC domains inside the fibers can be electrically switched upon application of an AC-electric field.

138. A New Type of Switchable Metallo-Supramolecular Gel

Shihu Wang and Elena E. Dormidontova, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Metallo-supramolecular gels have attracted considerable interest due to their self-healing properties and their ability to respond to external triggers, which enhances their potential for applications in many areas. Using Monte Carlo simulation we study a new type of `cis-trans` switchable metallo-supramolecular polymers based on 1:2 (transition) metal-ligand complexes, acting as chain extenders and 1:3 metal-ligand complexes representing branching points or crosslinks. We found that supramolecular polymers formed from `cis-` isomers possess a larger overall degree of association and a higher average molecular weight due to the formation of a larger fraction of 3:1 or 2:1 ligand-metal complexes compared to that for `trans-` isomers. As a result, formation of a metallo-supramolecular gel based on `cis-` metal-ligand complexes occurs at a lower oligomer concentration and within a wider range of metal-to-oligomer ratios. The resulting metallo-supramolecular gel exhibits a larger elastic modulus and a smaller mesh-size than the gel formed by `trans-`metal-ligand complexes. We demonstrate that an increase in the fraction of `trans-` isomers leads to a noticeable (sometimes non-linear) change of material properties and we predict the conditions when these changes can be observed experimentally. These results indicate the new opportunities of utilization of externally-triggered metallo-supramolecular polymers in the area of smart devices.

This work was supported by the NSF Career Award CHE-0348302

139. Poly(styrene) Degradation

Bob A. Howell, Center for Applications in Polymer Science and Department of Chemistry, Central Michigan University, Mount Pleasant, MI

General purpose poly(styrene) produced by conventional radical techniques is widely used in food packaging, particularly, as rigid, transparent containers for cookies, muffins, pastries, etc. Processing of the polymer and generation of packaging must be done under controlled conditions to prevent the impartation of a distinct and disagreeable odor/taste in the item packaged. What is the origin of this contamination? For the polymerization of styrene, termination occurs almost totally by radical coupling. This generates polymer which contains one head-to-head unit per chain. This might provide a defect point from which polymer degradation could be initiated. To examine this possibility a fully head-to-head poly(styrene) was generated by reduction of poly(2,3-diphenyl-1,3-butadine). The degradation of both polymers at 280° C was examined. Initial degradation is quite similar for the two. However, after a short initial period, degradation of the polymer produced by conventional radical techniques becomes very rapid. Degradation monitored by TG/GC/MS reveals that styrene monomer is formed as that only volatile product. This suggests that a low temperature (280° C), initial chain cleavage at the heat-to-head unit generates macroradicals which rapidly extrude styrene monomer.

140. Ice Templated Materials - Clay Aerogels and Beyond

Matthew D. Gawryla, Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH and David A. Schiraldi, Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Low density structural materials are important to many industries especially for their low thermal conductivity and weight savings. Clay aerogels and their composites are relatively new entrants into this arena and are fascinating due to their being created via an environmentally friendly ice templating process. As water freezes, the crystals expel any impurities and deposit them at the grain boundaries. Assuming the components are in high enough concentration, removing the water leaves behind a three dimensional structure which is effectively the negative of the frozen solution. The usefulness of these composites is derived from the microstructure, the properties of the constituent materials, and their interactions with one another. Polymer chemistry, molecular weight, and solubility are all tools we can use to tailor the properties of these materials to fit many applications. The effect of mold design, concentration and filler type will be discussed in terms of effect on modulus and thermal conductivity of select composites. Optical imaging tools used for rapid screening of structure will also be presented.

141. Towards the Synthesis of Amphiphilic Nanoparticles Using Crosslinked Polystyrenes

James S. Baker Jr. and Coleen Pugh, Department of Polymer Science, The University of Akron, Akron, OH

One of the current focuses in the field of polymer synthesis is the preparation of polymers having well-defined architectures. The goal of this project is to prepare amphiphilic nanorods so others can study the self-assembly of these particles into 2-D and 3-D structures. The nanoparticles will be composed of diblock copolymers of styrene derivatives, with each block having a different surface chemistry. For example, after crosslinking in a two-phase solvent system, poly(styrene)-`block`-poly(4-(oligooxyethylene)styrene) will result in a polymer nanoparticle having a hydrophobic lobe and a hydrophilic lobe. Upon heating above a threshold temperature, the crosslinking agent isomerizes and rapidly reacts to form dimers and oligomers. Under ultra-dilute conditions a polymer chain containing these functionalities can undergo intramolecular chain collapse to give a crosslinked, discrete particle. The polymers for this study are being prepared `via` controlled radical and living anionic polymerization. Phase separation of the blocks in a two-phase solvent system minimizes interblock crosslinking.

Functional Materials: Biofunctional Materials (2)

Organizer: Horst A. von Recum Case Western Reserve University, Cleveland, OH
Presider: Horst A. von Recum Case Western Reserve University, Cleveland, OH

Session Overview: This sesssion will cover all manner of materials either based on biological design, modified with biomolecules and/or used in biomedical applications. Applications include self-assembling materials, tissue engineering, and drug delivery.

142. Dissipative Particle Dynamics Simulations of Micelle Targeting Dynamics

Hadrian Djohari and Elena Dormidontova, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Polymeric nanoparticles have unique potential as vehicles for hydrophobic drugs and imaging agents. Nanoparticles can protect drugs during transport, increase their bioavailability, and remain innocuous inside the blood stream. Clinical trials have shown that targeted micelles, administered at the systemic level, can selectively accumulate in the biological target, thereby reducing the potential side effects of drug administration and increasing the efficiency of treatment.

In order to optimize nanoparticle design it is important to understand the local dynamics of polymeric micelle targeting to cell surface receptors, which is difficult to assess based on experiments only. We have applied dissipative particle dynamics (DPD) simulation method to investigate nanoparticle attachment dynamics, examining the effects of nanoparticle architecture (tether length, degree of functionalization), receptor density, and receptor distribution.

We show that micelle adsorption to the surface is strongly influenced by the ligand-receptor binding energy, micelle size, and receptor distribution on cell surface. We also observed that the kinetics of the nanoparticle attachment is driven by the ligand-receptor binding energy and changes nonlinearly with the number of ligands already bound to the surface. A sparse matrix of receptors on the surface will favor the adsorption of longer-reaching, bigger micelles. And finally, increasing the density of ligands on micelle surface enhances targeting efficiency.

143. Quantum Dot Surface Modification for Biomolecular Conjugation

Mikala Shremshock, Department of Chemistry, West Virginia University, Morgantown, WV and R. Lloyd Carroll, C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV

Quantum confined semiconductor nanoparticles, or quantum dots (QDs), are of great scientific interest for biological, engineering, and chemical applications. They have become important research materials in a variety of areas because of their unique and tunable optoelectronic properties, such as fluorescence and tunable bandgap size. Here, we have synthesized our own CdSe/ZnS core/shell QDs using a more environmentally benign reaction. As synthesized, the QDs bear hydrophobic organic surface ligands. This is problematic for biological applications where aqueous buffer solutions are used or for bottom-up assembly and immobilization of QD devices. To modify the surface and solubility properties of the QDs, two approaches have been explored: ligand exchange and polymeric encapsulation. Ligand exchange has been successfully demonstrated, providing buffer solubility as well as amine and carboxylic acid functional groups for the attachment of quenchers, fluorescent labels, peptides, and other targeting molecules. Polymeric encapsulation has been demonstrated with an amphiphilic polymer composed of random alkyl chains along a poly(acrylic acid) backbone. These systems provide higher buffer solubility and a greater number of acidic anchor points, at the expense of quantum dot size. These materials have been extensively characterized by X-Ray Photoelectron Spectroscopy, Dynamic Light Scattering, UV-VIS, Raman, and IR spectroscopy to determine composition, surface coverage, effective size and morphology, band edge shift, and photoluminescent quantum yield. Comparisons of the properties of each type of surfactant on QDs can then be utilized to determine the optimum ligand for biological, chemical, and technological applications.

144. Prussian Blue Nanoparticles: Novel Dual Agents for Magnetic Resonance Imaging and Drug Delivery

Eric Soehnlen, Mohammadreza Shokouhimehr, Songping Huang and Soumitra Basu, Department of Chemistry, Kent State University, Kent, OH

There is an unfulfilled need in the field of cancer treatment for new dual agents, which would provide health care specialists the ability to simultaneously image patients' cancerous tissues as well as treat the disease. Prussian Blue (ferric hexacyanoferrate) is a nontoxic FDA approved compound used clinically as an antidote for thallium and radioactive cesium poisoning. We have developed a simple method for the synthesis of biocompatible citrate coated Prussian blue nanoparticles (PBNP) with excellent size dispersion of ~25nm. Our preliminary studies show that PBNPs significantly shorten the T_1 relaxation time in aqueous solution demonstrating their potential use as T_1weighted Magnetic Resonance Imaging (MRI) contrast agents. In order for PBNPs to be concurrently utilized as drug delivery agents they must be capable of crossing the plasma membrane. To study intracellular uptake of the PBNP's, their surfaces were functionalized separately with the small molecule dyes fluorescein and Texas Red, as well as the antitumor agent doxorubicin. Confocal fluorescence imaging of HeLa cells treated with the functionalized nanoparticles show strong fluorescent signal in the cytoplasm suggesting intracellular uptake of the PBNPs. Additional proof of cellular uptake of the PBNPs is provided by ICP-OES analysis that quantitatively compares iron content of PBNP treated and untreated cells. HeLa cells treated with PBNPs show at least one hundred percent increase in iron content when compared to the untreated control. Functionalized PBNPs with both MRI contrast and drug delivery capabilities may become powerful dual agents for simultaneous cancer treatment and assessment of treatment effectiveness.

145. Biodegradable Functional Polymers for Drug Delivery

Abhishek Banerjee, William Storms and Coleen Pugh, Department of Polymer Science, University of Akron, Akron, OH

Biodegradable polymers have been used in biomedical applications as sutures and more recently as drug delivery systems. Drug delivery systems use amphiphilic block copolymers that self assemble into micelles above their critical micellar concentration. Such block copolymers typically use copolymers of lactic acid and glycolic acid as the hydrophobic part, and polyethylene glycol as the hydrophilic part of the amphiphile. These amphiphiles are capable of solubilizing hydrophobic drugs in aqueous media, thereby preventing premature drug degradation and premature drug precipitation. However, drug loading capabilities of such amphiphilic copolymers is limited due to the lack of functionalities on the main chain of the polymer. Our research deals with synthesizing potentially biodegradable functionalized co-polyesters. The functionalities on the back bone of the co-polyester present sites for drug attachment either directly, or with the aid of a spacer molecule. Such co-polyester can also be made amphiphilic with the attachment of polyethylene glycol chains on one end, which could allow it to assemble into micelles. We have found that these co-polyesters can form spherical particles in the range of 500 nm to 5 micron. The biodegradability of these co-polyesters can be tailored by varying the amount of glycolic acid and lactic acid in the co-polyester. Such functional and biodegradable polymeric materials could be used for making very interesting biofunctional materials.

146. Controllable Hydrolytic Degradation of Electrospun Biopolymer Scaffolds

Michael S. Spagnuolo and Lingyun Liu, University of Akron, Akron, OH

It is important to control the degradation rate of a tissue-engineered scaffold so that the scaffold will degrade in an appropriate matching rate as the tissue cells grow in. The focus of this study is to synthesize, characterize, and construct a detailed degradation profile for tissue engineering scaffolding that has been electrospun from several biopolymer blends. The two constituent polymers being used are L-Tyrosine based polyurethanes: PCL-HDI-DTH and PEG-HDI-DTH. Polymers vary by only their soft segments, which are formed from either polycaprolactone diol (PCL) or poly(ehtylene glycol) (PEG), with linear hexamethylene diisocyanate (HDI) used as the hard segment and desaminotyrosyl-tyrosine hexyl ester (DTH) used as the amino acid based-chain extender. The former is hydrophobic while the latter is moderately hydrophilic. It has been demonstrated in literature that the hydrolytic degradation of these two polymers is significantly different mostly because of their different hydophobicity. Blending the two extremes in the appropriate ratios in the electrospun biopolymer scaffolds allows for a more controlled degradation window with the ultimate goal of matching the scaffold degradation rate to the specific optimal growth rate of any number of cell types.

147. Degradable Microparticles for Protein Delivery

Nick X. Wang[1], Doug Bazdar[2], Scott Sieg[2] and Horst A. von Recum[1], (1)Department of Biomedical Engineering, Case Western Reserve University, Cleveland, OH, (2)Center for AIDS Research, Case Western Reserve University, Cleveland, OH

In HIV infections, homoeostasis of T-cells is dysregulated such that there is a depletion of CD4+ T-cells and a progressive loss of naïve CD4 and CD8+ T-cells.[1] Methodologies that can improve the function of some or all of these cells will likely enhance immune responsiveness in HIV infection. Interleukin-7 (IL-7) is a cytokine that has been shown to be critical in homeostatic expansion of naïve CD8+ and CD4+ cells in lymphopenic hosts.[2] In mice, daily injections of IL-7 boosted both CD4+ and CD8+ cell responses to immunization. Daily injections, however, are painful, inconvenient, and provide a frequent route for pathogen entry. We are developing a poly (D,L – lactide-co-glycolide) (PLGA) microparticle controlled release system to administer IL-7 in which a single injection of microparticles can provide therapeutic delivery of IL-7 from weeks to months.

IL-7 encapsulated PLGA microparticles were synthesized using a water/organic/water double emulsion method, release from the particles was then optimized using in vitro release studies. Therapeutic effectiveness was studied in mice. PLGA microparticles showed effective delivery of IL-7 for up to 3 weeks in vitro. These results were translated to in vivo delivery as well, which was followed for 9 days. Controlled release of IL-7 in mice demonstrated biological activity in both CD4+ and CD8+ T cells in mice, which was consistent with previously reported results using daily injections.

1. Bazdar, D.A.; Sieg, S.F. `J of Virology`. 2007, 81, (22), 12670-12674
2. Schluns, K.S.; Kieper, W.C.; Jameson, S.C.; Lefrancois, L; `Nature Immunology`, 2000, 1, (5), 426-432

148. Janus Fibers and Beyond…

Srijanani Bhaskar[1], Suparna Mandal[2] and Joerg Lahann[2], (1)Macromolecular Science and Engineering Program, University of Michigan, Ann Arbor, MI, (2)Department of Chemical Engineering, University of Michigan, Ann Arbor, MI

Because the local microstructure plays a pivotal role for many biological functions, a wide range of methods have been developed to design precisely engineered substrates for both fundamental biological studies and biotechnological applications. Herein, we use electrohydrodynamic co-spinning of two or more polymer solutions to fabricate microfibers made from poly(lactide-co-glycolide) polymers, which are comprised of several distinguishable compartments. Orientation, size, and arrangement of individual fiber compartments were controlled in a highly predictable fashion. When aligned multicompartmental fibers are modified via spatially controlled peptide immobilization, three-dimensional fiber scaffolds with precisely engineered, micrometer-scale patterns can be obtained. These unique scaffolds exhibited highly selective cell guidance ($p \leq 0.05$) at spatial resolutions (< 10 mm) that have been, so far, exclusively reserved for flat substrates.) Multicompartmental three dimensional tissue engineering scaffolds could potentially mimic in vivo cellular environments more closely by supporting co-organization of different cell types.

149. Reversible Temperature Induced Nanoparticle Formation by Elastin-Like Polypeptide Trimers

Ali Ghoorchian, James T. Cole and Nolan B. Holland, Department of Chemical & Biomedical Engineering, Cleveland State University, Cleveland, OH

We have designed and expressed environmentally responsive polypeptides that reversibly self-assemble into nanoparticles of uniform size. The polypeptides consist of elastin-like polypeptide (ELP) pentapeptide repeats of GVGVP followed by a trimer-forming oligomerization sequence at the carboxy-terminus. After expression in `E. coli` and purification by thermal cycling, the polypeptide spontaneously folds as a homotrimer that is soluble in aqueous solution. Upon heating above a critical temperature, hydrophobic interactions dominate in the ELP and the trimers self-assemble into micellar particles with the hydrophobic ELP tails stabilized by the charged oligomerization domains which act as head groups. The micelles are stable in solution without forming any larger aggregate up to temperatures well above the ELP transition temperature and even higher than the oligomerization domain stability temperature. This is unlike typical ELP polymers which aggregate and phase separate into a coacervate at the transition temperature. The transition temperature for assembly of these nanoparticles can be tuned by substituting amino acids of differing hydrophobicity for valine residues in the GVGVP repeat sequences. Alternatively the transition can be controlled by changes in pH. By varying the length and composition of the polypeptides, we can control the size of the assembly and the transition stimuli necessary for the assemble into nanoscale particles, which makes them very good candidates for designing targeted drug delivery carriers. They can also become an approach for solving enduring questions regarding the structure of the folded ELP.

Functional Materials: Membranes and Layered Systems (2)

Organizer: Peter Pintauro Vanderbilt University
Organizer: Jeffrey A. Gray Ohio Northern University, Ada, OH
Presider: Jeffrey A. Gray Ohio Northern University, Ada, OH
Presider: Peter Pintauro Vanderbilt University

150. Multilayer Polymer Films for Photonic Applications

Kenneth D. Singer, Departement of Physics, Case Western Reserve University, Clevland, OH

Roll-to-roll manufacture has been an important goal for realizing low-cost photonic and electronic devices. We have been developing a process for producing photonic devices based on a melt-process, co-extrusion technique for making active photonic devices. The process produces A-B multilayer polymer films of up to thousands of layers for applications as photonic crystals and other multilayer optics applications. We have demonstrated low-threshold, high efficiency surface-emitting distributed Bragg reflector lasers that have well-defined longitudinal and transverse modes. More recently, we have produced surface-emitting distributed feedback lasers that can be manufactured in a single roll to roll process. We will also describe additional applications in both passive and active photonic devices.

151. Confined Crystallization In Forced Assembly Polymer Nanolayers

Michael Ponting[1], H.P. Wang[1], J. Keum[1], A. Hiltner[1], Benny Freeman[2] and E. Baer[1], (1)Deparment of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, (2)Department of Chemical Engineering, University of Texas at Austin, Austin, TX

Confinement induced orientation of semi-crystalline polyethylene oxide (PEO) and polycaprolactone (PCL) nanolayers was examined using innovative “forced assembly” multilayer coextrusion. PEO or PCL layer thicknesses ranging from microns to 20 nanometers where coextruded against amorphous polymer layers to examine the affect spatial confinement on polymer crystallization. When semi-crystalline polymer layer thicknesses were decreased below the micron scale, PEO and PCL lamellae crystal orientation changed from bulk-like spherulitic morphology to high-aspect ratio lamellae oriented parallel to the layer boundary. Further reduction of crystalline layer thickness to 20 nanometers produced a single lamellae crystal layer resulting in orders of magnitude decrease in the polymer layer gas permeability. Confinement induced changes in the semi-crystalline polymer morphology were confirmed with WAXS/SAXS and AFM cross-sections micrographs of the multilayered polymer film. Investigations into the affects of polymer film crystallization temperature and amorphous confining layer material were examined to further explore the phenomena of confined crystallization in coextruded polymer nanolayers.

152. Dielectric Properties of Micro and Nanolayered PC/PVDF Films

Matt Mackey[1], Anne Hiltner[1], Eric Baer[1], Lionel Flandin[2], Mason Wolak[3] and Jim Shirk[3], (1)Department of Macromolecular Science and Engineering, CWRU, Cleveland, OH, (2)LMOPS-UMR 5041 CNRS Université de Savoie, F-73376 Le Bourget Du Lac Cedex, France, (3)US Naval Research Labatory, Washington, DC

There is a need in electronic systems and pulsed power applications for capacitors with high energy density. For large scale capacitor production, advantages of polymers over inorganics include excellent processability and high energy to weight ratio. Current state-of-the-art polymeric capacitors (3 J/cm^3) are however limited in that a tradeoff exists between energy density and loss. From a material standpoint, the energy density improves with increasing dielectric constant and/or breakdown strength, whereas the loss may be diminished by reducing dielectric losses and high field polarization hysteresis. Our approach to improve polymer film capacitors is to combine, through microlayer coextrusion, two polymers with complimentary properties: one with a high dielectric constant (polyvinylidene fluoride-hexafluoropropylene) and one with a high breakdown strength (polycarbonate). As opposed to the monolith controls, multilayered films with various numbers of layers and compositions exhibit treeing patterns that hinder the breakdown process. Consequently substantially enhanced breakdown strengths are measured in the mutilayered films. In addition, reduction of polarization hysteresis arises from the effect of layer confinement on the structure. This work demonstrates that multilayering two polymers synergistically improves the dielectric properties for capacitor applications. Energy densities of up to 13 J/cm^3 are measured while maintaining very low losses. Using the understanding gained from these systems, selection and optimization of future layered structures can be carried out to obtain even higher energy densities and lower dielectric losses.

153. Layered Systems Based On Composites of Poly(propylene-graft-maleic anhydride)/Phosphate Glass with Excellent Gas Barrier Properties

Mohit Gupta, Yijian Lin, Taneisha Deans, Eric Baer, Anne Hiltner and David Schiraldi, Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

The ability to produce alternating (A-B-A-B) polymer films with individual layer thicknesses in the 10 nm - 100 μm range, using a robust extrusion process is being used within the NSF Center for Layered Polymeric Systems to produce high performance materials and devices. When the “B” layers of such a layered film are composed of a poly(propylene-graft-maleic anhydride)/phosphate glass (Pglass) composite, the layered films upon biaxial orientation can exhibit percolation of high barrier filler resulting in reduction in gas permeation by three orders of magnitude. This unprecedented reduction in oxygen permeability is attributed in part to the high volume fraction (up to 20 vol %) of highly aligned Pglass platelets in the polymer matrix resembling a brick wall nanostructure. Biaxially oriented films with 20 vol % Pglass content demonstrated a microstructure resembling alternating layers of pure Pglass and polymer. Structural models for permeability indicated that enhanced barrier arose primarily from increased tortuosity of the diffusion pathway provided by the aligned high aspect ratio platelets. Aspect ratios ranging from 40 to 180 were obtained by fitting the experimental data to the models. Mechanical tests revealed that presence of Pglass platelets increased the modulus of the multilayer composites by as much as 3x, while reducing the elongation at break only slightly. With an optical transparency between 65-85 %, and good flexibility, these films stand out as good candidates for a variety of packaging applications.

154. Mechanical Properties of Polymer/Clay Aerogels as Function of Polymer and Electrolyte Loadings

Saeed Alhassan[1], Syed Qutubuddin[1] and David A. Schiraldi[2], (1)Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH, (2)Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Clay aerogel is an open-cell cellular solid, which is produced using expandable clay aqueous dispersion followed by freeze-drying. Properties of cellular solids; such as density, depend on processing conditions and starting material composition. The effects of these factors on the density and mechanical properties of the aerogels were investigated. Polyvinyl alcohol (PvOH) and sodium chloride (NaCl) were chosen as model polymer and electrolyte, respectively. The density of the aerogel plays a pivotal role in determining the mechanical behavior. Adding polymer increases the aerogel density and hence improves the compressive modulus and strength. However, the addition of electrolyte increases the compressive modulus and strength at low polymer loading (<2% w/w) and has negligible effect at high polymer loading (>3% w/w).

155. Computational Studies of CO2 Interaction with Functionalized Gamma-Al2O3 Surfaces

Janice A. Steckel, U.S. Departement of Energy, National Energy Technology Laboratory, Pittsburgh, PA

Development of low-cost, efficient membrane-based gas separation techniques capable of functioning in flue gas conditions are a key step in achieveing CO_2 capture from existing power generation plants. Inorganic membranes possess the desirable qualities of high permeance and low cost, and the functionalization of such membranes shows promise in terms of improving CO_2 selectivity. The interaction of CO_2 with the surfaces of bare, hydroxylated and amine-functionalized gamma-Al_2O_3 has been modeled using density functional theory (DFT) calculations. While interactions of CO_2 with the bare surface are quite strong, binding sites are blocked by hydroxyl groups under most conditions. Models are presented for the interaction of CO_2 with the functionalized surface.

General Catalysis (2)

Sponsor: Saint-Gobain NorPro
Organizer: Dave VanderWiel Saint-Gobain NorPro, Stow, OH
Organizer: Stephen Dahar Saint-Gobain NorPro, Stow, OH
Presider: Dave VanderWiel Saint-Gobain NorPro, Stow, OH
Presider: Stephen Dahar Saint-Gobain NorPro, Stow, OH

Session Overview: The General Catalysis Symposium will focus on novel catalytic materials for energy and environmental applications, including functional catalytic structures, adsorption & surface phenomena, catalysis in novel reaction systems, developments in gas-to-liquids catalyst materials, catalyst support materials, high selectivity catalysts, future trends in catalysis and related topics. Speakers will include academic and industry researchers, including invited talks from throughout the region.

156. The Next Generation of Industrial Catalysts: Challenges and Opportunities

Saeed Alerasool, Research Director, Research and Development, BASF Corporation, Iselin, NJ

Recent global changes have created both challenges and opportunities for heterogeneous catalysis. Rising crude oil and natural gas prices coupled with ever-tightening legislative mandates for cleaner fuels have increased the urgency for developing novel catalytic processes for producing various petrochemical products. These new catalytic processes will be more efficient, involve fewer steps and use more abundant feedstock. The primary focus of this presentation is to describe a number of BASF's new technologies as well as key initiatives designed to meet these challenges.

157. Fischer-Tropsch Synthesis: Reaction Mechanism for Iron and Cobalt Catalysts

Burtron H. Davis, Center for Applied Energy Research, University of Kentucky, Lexington, KY

The initial mechanism advanced by Fischer was the bulk carbide formed and was subsequently hydrogenated to alkanes; this mechanism was replaced about 1950 by the oxygenate intermediate mechanism favored by Storch and Emmett. With the introduction of surface science instrumentation in the 1970s, the surface carbide mechanism became almost universally accepted. Our studies using radioative and stable isotopes support a return to the oxygenate mechanism, at least for the iron catalyst. Our results obtained using isotopic tracers will be described.

158. Olefins by High Intensity Oxidation in Microchannel Reactors

Terry Mazanec, Chief Scientist, Velocys, Inc., Plain City, OH

Olefins, including ethylene and propylene, are among the highest volume chemicals in the world. The conventional route to olefins is steam cracking, which requires a large capital investment and is highly energy intensive. Alternative oxidative routes (from ethane or propane) have been investigated due to their potential to greatly reduce the equipment size and energy consumption of the process. However, the promise of an oxidative process has long been thwarted by limitations of conventional processing equipment to control the temperature inside the reactor. Microchannel reactor architecture offers a solution to the heat management challenge and therefore holds the potential to substantially reduce the cost to produce olefins.

Catalytic microchannel olefin reactors provide important process benefits. The intensified heat exchange possible in microchannels permits rapid, efficient pre-heating and quenching, both of which minimize side reactions. And precise intra-reactor mixing maintains reactant concentrations near the stoichiometric optimum to improve selectivity to the desired olefin product. Excellent heat exchange within the microchannel can eliminate the need for separate heat exchangers, which present problems of corrosion and fouling in conventional systems. And the use of oxygen rather than air precludes the formation of NOx, a major source of acid rain.

This presentation will describe the development efforts on a DOE-sponsored joint program with Velocys, Dow Chemical and Pacific Northwest National Laboratory to develop the microchannel approach to oxidative olefin production, including scale-up to a multi-channel device that is scaleable to a commercial scale.

159. Preparation, Properties and Selected Applications of Catalyst Supports

Thomas Szymanski, Saint-Gobain NorPro, Stow, OH

Preparation, Properties and Selected Applications of Catalyst Supports

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As feedstock and energy prices increase, petrochemical producers struggle to balance the mandate that they simultaneously increase production while using less energy and producing fewer byproducts. These increasingly severe conditions will often require new processes and/or new catalyst-carrier systems. The stringent demands placed on these carrier-catalyst systems will cause even more emphasis to be placed on quality issues. This paper will survey various methods used to prepare engineered porous ceramic materials for hydrocarbon conversion processes and discuss some applications.

160. Hydrothermal Synthesis of Advanced Materials for Catalytic Applications

Wojciech Suchanek, PhD, Sawyer Technical Materials, LLC, Eastlake, OH and Juan M. Garces, Consultant, Midland, MI

This presentation briefly reviews hydrothermal synthesis of ceramic materials for catalytic applications and shows how understanding the underlying physico-chemical processes occurring in the aqueous solution can be used for engineering hydrothermal crystallization processes. The overview covers the current status of hydrothermal technology for inorganic materials with respect to types of materials prepared and ability to control the process, as viewed from commercial manufacturing perspective. General discussion is supported with specific examples derived from own research and industrial production in our hydrothermal plant in Eastlake, OH (α-Al_2O_3, $ZnAl_2O_4$ spinel, and ZnO powders, carbon nanotubes, zeolites, α-quartz single crystals, etc.). Hydrothermal crystallization processes afford excellent control of morphology, size, agglomeration, and chemical compositions of inorganic materials, which in turn generate unique performances of catalysts and catalytic supports.

Special emphasis will be given to hydrothermally synthesized alpha alumina (α-Al_2O_3) powders with a variety of morphologies (equiaxed, platelets, whiskers, nano-sheets, nano-needles), crystallite sizes in the range of 10 nm – 40 mm, narrow particle size distributions, controlled agglomeration, chemical purity up to 99.98%, high phase purity (100% α-Al_2O_3), and BET surface areas up to 40 m^2/g (stable at high temperatures). Several examples of catalytic supports comprising α-Al_2O_3 ceramics and transition aluminas/α-Al_2O_3 composites will be provided. These materials exhibit unique combination of well-controlled high pore volumes and BET surface areas, multi-modal pore size distributions, and high strength due to the use of hydrothermally synthesized high-purity α-Al_2O_3 powders and α-Al_2O_3/γ-AlOOH powder mixtures as starting materials.

161. Hydroxylation of Phenol with Hydrogen Peroxide Over ZnFe2O4

Jianfeng Yu[1], Hui Shao[1], Chengyang Tie[1], Siyu Tu[1], Wenxiang Zhang[2] and Tonghao Wu[2], (1)Department of Chemistry, The Ohio-State University, Columbus, OH, (2)College of Chemistry, Jilin University, Changchun, China

The catalytic activity of zinc ferrite with spinel structure in the hydroxylation of phenol with 30% aqueous hydrogen peroxide using water as the solvent was studied, and the effects of the various conditions were summarized. On the basis of the results of XRD, Mössbauer, and in situ IR spectra studies, the composition of the catalyst and the possible reactive intermediate over the catalyst was discussed. The mechanism of phenol hydroxylation with hydrogen peroxide catalyzed by iron(III) generally accepted is Fenton processes. But we also observed an intermediate over the surface of the catalyst. In the range of $800\sim1600 cm^{-1}$, the characteristic peaks of $ZnFe_2O_4$ were detected at 1580.0, 1387.5, and 870.7 cm^{-1}. When 30% aq. H_2O_2 was introduced to the system, the former peaks were unchanged, but new peaks appeared at 1225.0, 1118.0 and 956.3cm^{-1} , which were associated with the results of the chemical effect between the catalyst and H_2O_2. In fact, when the H_2O_2 was replaced with H_2O, no new peaks appeared.

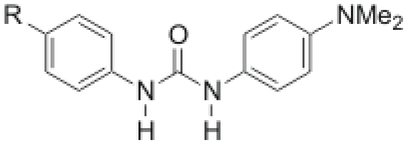
Women in Electrochemistry (2)

Organizer: Heidi B. Martin Case Western Reserve University, Cleveland, OH
Organizer: Carol Korzeniewski Texas Tech University, Lubbock, TX
Organizer: Irina Serebrennikova Energizer, Westlake, OH
Presider: Irina Serebrennikova Energizer, Westlake, OH
Presider: Carol Korzeniewski Texas Tech University, Lubbock, TX
Presider: Heidi B. Martin Case Western Reserve University, Cleveland, OH

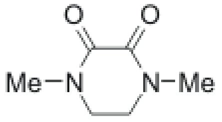
162. Very Strong Redox-Dependent Hydrogen Bonding Between a Bis-Dimethylaminophenylurea and a Cyclic Diamide

Diane K. Smith, Karina Kangas and Jessica E. Woods, Department of Chemistry and Biochemistry, San Diego State University, San Diego, CA

Over the past decade, it has been shown that it is possible to selectively and significantly perturb the strength of hydrogen bonding between organic molecules using electrochemistry. However, although both reduction and oxidation reactions have been used, reductions have generally proven more successful. Recently, we reported the observation of strong oxidation-based, redox-dependent hydrogen bonding between the electroactive urea 1 and the cyclic diamide 3 in CH_2Cl_2 with NBu_4 $B(C_6F_5)_4$ as the electrolyte. This behavior can be deduced from the large negative shift in the $E_{1/2}$ of the $1^{0/+1}$ CV wave in the presence of 3. CV simulations indicate there is a greater than 2000-fold increase in binding strength upon oxidation of 1. In this paper we report similar studies with the bis-dimethylaminophenyl derivative, 2, which can undergo two reversible oxidations forming a bi-radical. As with 1, addition of 3 to 2 results in the first oxidation shifting negative. A maximum shift of about -200 mV is observed after 50 equivalents, very similar to what is seen with 1. The second CV wave of 2 also shifts negative by a similar amount. However, this wave reaches the maximum shift after only 1 equivalent of 3 has been added. This behavior indicates that all of the 2^+ species is complexed with one equivalent of 3. The observation of the maximum shift being reached with only one equivalent of a non-ionic guest is rare, and points to the very strong hydrogen bonding occurring in this system.



1 R=H **2** R=NMe$_2$



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163. Conductive Diamond: One Material for Both Neurosensing and Neural Stimulating Electrodes?

Heidi B. Martin, Chemical Engineering, Case Western Reserve University, Cleveland, OH

The need for robust, versatile, implantable electrodes is increasingly important as functional electrical stimulation and neurosensing technologies continue to expand their range of benefit to human health. Stimulating electrodes may be pushed to their limits to apply higher currents while still avoiding tissue and electrode damage. Co-implantation of neurotransmitter sensing electrodes with stimulators may be desirable, to provide chemical feedback to aid in positioning and programming of the stimulators.

Conductive diamond provides unique opportunity to integrate sensing and stimulation in the same device. Diamond may expand neural stimulation capabilities by avoiding side reactions that lead to tissue damage and by providing long-term stability. Diamond electrodes possess exceptional electrochemical properties, providing advantages for neurochemical sensing; new chemistries and lower analyte concentrations may be investigated because of its extremely wide potential window of water stability and low baseline current, respectively. This presentation focuses on fabrication and characterization of functionalized diamond-film electrodes and application toward (a) stimulation of neural activity (b) in vitro detection of neurotransmitters and neuromodulators, and (c) detection of electrical activity. Unique fabrication approaches to render the electrodes flexible will also be presented.

164. Optimization of Conducting Polymers for Neurological Applications

Anthony D. Kammerich[1], **J. Faye Rubinson**[1], Forcelli Patrick[2], Karen N. Gale[2] and Cameron Sweeney[1], (1)Department of Chemistry, Georgetown University, Washington, DC, (2)Department of Pharmacology, Georgetown University, Washington, DC

Several conducting polymer electrodes have been examined for their promise for deep brain stimulation (DBS), a therapy used to minimize the effects of several neurological disorders such as Parkinson’s disease. The monomers 3-methylthiophene (3MT), 3,4-ethylenedioxythiophene (EDOT), and N-methylpyrrole (NMP), were electrochemically polymerized as films on the surface of platinum electrodes. Polymerization has been carried out using two different approaches- both a standard cell for films and a flow cell for films and fibers. The conditions for the polymerization have been varied in order to determine optimal parameters to create a film with improved biocompatibility t while maintaining good electrochemical properties. After the ideal potentials and polymerization times to create thin films were determined, the films were characterized by SEM, Raman microspectroscopy, and cyclic voltammetry. SEM was used to determine the surface texture of the films under high magnification,and to measure the thickness of the films. Raman spectroscopy was empolyed to confirm the formation of the desired polymers and, in some cases to measure the doping level, while cyclic voltammetry provided valuable information about the electrochemical properties of the films. After the electrode fabrication parameters were optimized, the electrodes were tested `in vivo` in rats. Electrodes were implanted for various periods of times, up to 14 days, after which the animals were sacrificed and brain tissue sections examined for physical damage and immune response around the implantation site. Preliminary data has indicated the greatest improvement in biocompatibility thus far has been accomplished with P3MT.

165. Electrochemical Peptide-Based Sensor for the Detection of Anti-HIV Antibodies

Rebecca Y. Lai, Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE

A number of reagentless, electrochemical sensors based on the target-induced folding or unfolding of electrode-bound oligonucleotides (e.g. DNA, aptamers) have been developed in recent years; however, a comparable peptide-based sensing technology has yet to be realized. One advantage of a protein sensor is the greater accessibility of a protein-based target compared to pathogen DNA or RNA, which is often sequestered within the intact infectious agent. In addition, many proteins have higher concentrations than DNA or RNA in common clinical samples, such as serum. Here we report a reagentless, electrochemical peptide-based (E-PB) sensor for the detection of HIV. This E-PB sensor consists of a methylene blue-labeled peptide covalently attached via thiol-gold chemistry to a gold disk electrode. The recognition peptide we employ is a highly antigenic epitope from the HIV-1 capsid protein p24. In the absence of target, the peptide probe is unstructured and highly flexible, allowing efficient electron transfer to and from the redox label. Upon binding to the target protein, the folded peptide structure forces the redox label away from the electrode, obstructing electron transfer and therefore producing a readily detectable reduction in methylene blue current. Our results show that the E-PB sensor responds specifically to its antibody target (anti-p24 antibodies) in a concentration-dependent manner. Furthermore, we have investigated the sensor response in both direct and alternating current voltammetry and the results highlight the differences between the two electrochemical techniques as sensor interrogation methods.

166. Sphere Segment Void Structures: a Reproducible SERS Substrate for Electrochemical Studies

Andrea E. Russell, Prof.[1], Suzanne H. Pelfrey[1], Jon Speed[1], Sumeet Mahajan[1], Philip N. Bartlett[1] and Jeremy J. Baumberg[2], (1)School of Chemistry, University of Southampton, Southampton, United Kingdom, (2)Department of Physics, University of Cambridge, Cambridge, United Kingdom

We have recently shown that tailored surfaces prepared by electrodeposition through self-assembled colloidal crystal templates of uniform polystyrene spheres, now called sphere segment void surfaces, provide remarkably tunable and reproducible surfaces for Surface Enhanced Raman Spectroscopy. By careful selection of the diameter of the template spheres and thickness of the metal film, the plasmon modes of the surfaces may be selected to tune the surface to obtain the optimal enhancement for laser excitation wavelengths from near-IR (1064 nm) through to the visible (e.g. 633 nm) and now down to the UV (325 nm). In this paper the application of such substrates to obtain reproducible SERS of adsorbed species on electrode surfaces will be presented.

167. Electrochemical Seed-Mediated Growth of Gold Nanorods

Lina , G. Abdelmoti, Department of chemistry, University of louisville, Louisville, KY

Here we describe the synthesis of gold nanorods (NRs) by electrochemical deposition of gold onto mercaptopropyl-trimethoxysilane–functionalized indium tin oxide electrode coated with gold nanoparticles (ITO/MPTMS/AuNP) from a solution containing 2.5 x 10^{-4} M $AuCl_{4-}$ and 0.1 M cetyltrimethylammonium bromide (CTAB). The method is similar chemical synthesis of Au NRs, except that we replace the chemical reducing agent (ascorbic acid) with electrochemical potential. We varied the potential from -0.30 V to 0.50 V and deposited gold for 30 to 120 minutes. The potential for gold deposition occurs at 0.30 V or lower and 0.40 V or lower for ITO/MPTMS and ITO/MPTMS/AuNP respectively. Gold deposits at more positive potentials on ITO/MPTMS/AuNP because the AuNP catalyzes the Au depostion process. Most of the gold features on the ITO/MPTMS surface at all potentials were spherical particles or snowflake structures, while those on the ITO/MPTMS/AuNP surface depended on the electrode potential. Below 0.27 V, the structures were mostly spherical particles. Between (0.30 - 0.35V), a significant amount of Au NRs exist on the surface as well as spherical, hexagonal- and triangular-shaped particles. The applied potential controls the rate of gold deposition, which in turn affects the gold nanostructure size and morphology. We found that the Au NR yield (3 -12%) and average length (120 – 420 nm) depends on the potential and deposition time. This work is important for understanding the effect of reduction potential on the growth of gold nanostructures, which could lead to synthetic control of gold particles with desired optical and electrical properties.

168. Electrochemical Approach for Fabricating Devices for Sensing or Molecular Electronics Applications

Radhika Dasari and Zamborini Francis P, Department of Chemistry, University of Louisville, Louisville, KY

Here we describe a simple electrochemical approach for fabricating Electrode/metal nanowire/molecule or polymer/Electrode junctions for sensing or molecular electronics applications. The general procedure involves depositing a thin film (self assembled monolayer or polymer) on one electrode (E1) and electrodepositing an Ag metal nanowire (NW) on a second electrode (E2) 5-10 µm away from E1. Under appropriate deposition conditions, Ag NWs grow from E2 and cross over to E1, forming a E1/(molecule or polymer)/ Ag NW/ E2 junction. We controlled the junction resistance by 1) electrodepositing polyphenol of varied thickness on E1, 2) assembling alkanethiols of varying chain length on E1, and 3) Chemically dissolving the Ag NWs. We functionalized Ag NWs at high resistance E1/polyphenol/AgNW/E2 junctions with Pd nanoparticles and studied their sensing properties. They responded fast and reversibly to H_2 concentrations as low as 0.11% in a nitrogen carrier gas by a resistance decrease due to volume expansion of the nanoparticles. Future experiments will involve the assembly of molecules on E1 that exhibit photo- or redox-switchable electronic behaviour. Our strategy is promosing for forming simple, reproducible and miniaturized molecular electronics and sensing devices electrochemically at microgap electrodes with a wide range of potential applications.

ECS/YCES Graduate Student Research Posters

Sponsor: Cleveland Section of the Electrochemical Society (ECS) and Yeager Center for Electrochemical Sciences (YCES)
Organizer: Jeffrey Halpern Case Western Reserve University, Cleveland, OH
Organizer: Mike Nichols John Carroll University, University Heights, OH
Organizer: Mark J. Waner John Carroll University, University Heights, OH

Session Overview: This poster session is open to graduate student posters in any area of electrochemistry. Presenters are automatically entered into the poster competition hosted by the Cleveland Section of the Electrochemical Society and Yeager Center for Electrochemical Sciences. Two winners stand to receive grants of $500 (1st place) and $300 (2nd place) towards travel expenses to participate in the Fall 2009 or Spring 2010 Meetings of the Electrochemical Society.

169. Detecting Liver Disease by Determining Total Bile Acid Levels Using a Disposable Screen-Printed Iridium-Carbon Sensor

Brandon Bartling, Chemical Engineering, Case Western Reserve University, Cleveland, OH

Liver disease is a problem that affects millions of people every year. Liver diseases such as hepatitis and cirrhosis is a world-wide problem but often show up in areas of the world that are economically disadvantaged. In these conditions, knowing that the patient is suffering from liver disease in the early stages can lead to greater success in treatment and reduction in the spread of the disease. Biomarkers have seen a rise in interest as and effective way to monitor diseases. Once such biomarker, total bile acid, has been shown to correlate well with the presence of liver disease. In this work we present a cheap and disposable sensor that can accurately detect levels of total bile acid in solution. The sensor operates at the low potential of +0.27V so that interference from other species is minimized. Influence of environmental variable such as pH, temperature and physiological fluid is explored. The conclusion taken from the research shows that the sensor provides a viable method to detect the total bile acid levels of cholic, taurocholic and taurochenodeoxycholic acid over the target range of 0 to 200 micromol/L.

170. Selenium: a Non-Precious Metal Cathode Catalyst for Oxygen Reduction

Kiera Kurak and Alfred B. Anderson, Department of Chemistry, Case Western Reserve University, Cleveland, OH

Replacements are needed for platinum in fuel cell catalysts to increase efficiency and to lower the cost. From voltammetric studies, trigonal phase selenium nanotubes, which are bundles of hexagonally-packed helical chains, have been found stable in acid with a double layer region extending from -0.2V (SHE) to ~0.7V. This is similar to platinum’s ~0.4V to ~0.7V double layer region, and may present the possibility for oxygen reduction activity. In this study, we present a theoretical analysis of proposed oxygen reduction mechanisms over trigonal Se. The reversible potentials for the four one-electron reduction steps are determined using calculated adsorption energies for the intermediates in a linear Gibbs energy relationship. The results suggest possible good electrocatalytic activity toward oxygen reduction.

171. Peptide-Conducting Materials: Synthesis and Characterization

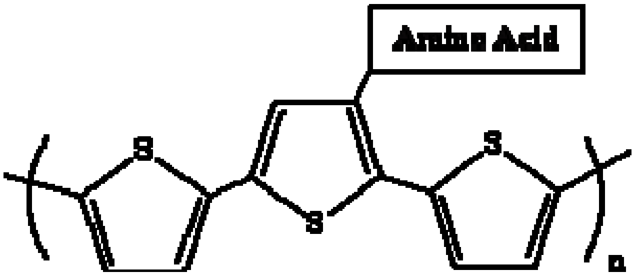
Christopher D. McTiernan, B.Sc. Biochemistry and M'hamed Chahma, B.Sc., M.Sc., Ph.D., Chemistry and Biochemistry, Laurentian University, Sudbury, ON, Canada

The objective of this research is to develop a new methodology for the immobilization of biomolecules such as amino acids onto solid conducting surfaces, which can be used as electrochemical biosensors. The proposed strategy aims at protecting the electrode through the use of a thin film of desired recognition biomolecule. This indirect approach to surface modification will help overcome the drawbacks associated with the adsorption of organic or bioorganic molecules on the conducting surface.

In the current research it has been seen that 2,5-dibromo-3-thiophene carboxylic acid and acetic acid in the presence of DCC and HOBt will afford the corresponding dibrominated thiophene-CO_2Bt. The latter further reacts with amino acids, to yield the corresponding amino acid functionalized thiophenes linked by an amide group.

The dibrominated monomers were then utilized in a stille coupling reaction with 2-tributylstannyl thiophene and a $Pd(Ph_3)_4$ catalyst to give the corresponding amino acid functionalized terthiophenes.

The progress in the synthesis and electrochemical/ chemical characterization of the monomers and corresponding polymers will be discussed.



172. Novel Polyether Suppressors Enabling Copper Metallization of High Aspect Ratio Interconnects

Julie Mendez and Uziel Landau, Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH

The effectiveness of the electroplating process for copper metallization of semiconductor interconnects hinges on the ability to generate void-free fill of sub-micron features. This is achieved through "bottom-up" plating, controlled by an additive mixture consisting typically of ppm quantities of chloride ions, a polyether, [conventionally, polyethylene glycol (PEG)], and an organic sulfur compound, [e.g., bis(3-sulfopropyl) disulfide (SPS)]. The polyether, a deposition suppressor, is a large molecule which undergoes diffusion-limited transport towards the via bottom and primarily adsorbs and inhibits deposition at the feature rim, the upper portion of the sidewalls, and wafer top surface. The faster diffusing SPS, a deposition enhancer, preferentially adsorbs on the via bottom, accelerating plating there. Due to competitive adsorption, SPS displaces the polyether as time progresses, leading eventually to enhanced deposition at the wafer surface and the feature sidewalls. Void-free bottom-up fill in aggressive interconnect geometries, i.e., aspect ratio exceeding 20, requires suppression stronger than that provided by the conventionally used PEG. Reported here are polarization studies of copper electrodeposition in the presence of several polyethers which heretofore have not been studied in the context of bottom-up fill. A number of these compounds (including polyoxyethylated β-naphthol and polyoxyethylene lauryl ether) exhibit superior inhibition, thus enabling the bottom-up fill of high aspect ratio features which cannot be metalized by PEG. Plating experiments confirm the advantage provided by these additives. A first-order scaling model which predicts the bottom-up fill efficacy is also presented. The authors acknowledge support from Intel Corporation and collaboration with Rohan Akolkar from Intel.

173. Spatially Averaging Electrodes

Disha Sheth, Richard Diefes and Miklos Gratzl, PhD, Biomedical Engineering, Case Western Reserve University, Cleveland, OH

Quantitative analyses of microliter samples have been successfully performed in our laboratory using diffusional reagent delivery with both optical and electrochemical end point detections. Though the sample drop is inhomogenenous during diffusional delivery, the equivalence point of microtitration can be indicated correctly when average concentration is monitored, as in the case of optical detection. As electrodes are not capable of sensing bulk concentration, for correct electrochemical end point indication stirring is necessary. In this work we introduce the concept of "spatially averaging electrodes" (SAE) that by virtue of their design can report bulk average concentrations for inhomogeneous samples without the need for stirring. The shape and dimensions of these electrodes are derived by taking into account the size of the sample and the type of concentration distribution. Actual concentration distributions are not required to be known for this approach to work. Here, we compare Potassium Ferricyanide [$K_3Fe(CN)_6$] differential peak currents obtained by a SAE spiral electrode designed for samples with radially symmetric concentration distribution, and microdisc and line electrodes during $K_3Fe(CN)_6$ delivery into a 1μL drop with and without stirring. We found that the differential peak current measured with the spiral electrode without stirring is within 0.8% of that obtained with stirring. This difference is significantly greater for the line and the microdisc electrodes: 6.3% and 10.8%, respectively. Therefore, the designed 2D SAE can be used for measuring 3D averaged concentration in applications like diffusional microtitration, lab-on-a-chip, and microfluidics where sample stirring is not readily available.

174. Oxidation of Glycerol: Electrochemical Studies and Use in Fuel Cells

Philip A. Stuckey and Thomas A. Zawodzinski, Department of Chemical Engineering & Case Applied Power Institute, Case Western Reserve University, Cleveland, OH

The ability to oxidize higher order polyols, (e.g. glycerol) would have a dramatic impact on the fuel cell market. Glycerol, a waste product of biodiesel production, currently has a cost associated with its disposal. In this context, we seek to develop a capability for electrochemical oxidation of glycerol to turn waste into a fuel. To make this process as efficient as possible and to identify suitable catalysts, we are studying the mechanism of this oxidation process. Substantial work has been done on electrochemical oxidation of oxygenated compounds such as methanol, ethanol and so on. Methanol, and 'methanol carriers' such as tri-methoxy methane, though less active than hydrogen, are relatively easily oxidized on Pt-Ru alloys in acid media. Compounds with C-C bonds, however, offer significant challenges to break those bonds.

Cyclic voltammetry (CV) shows catalytic poisoning and helps identify the steps in the oxidation mechanism. CVs were collected in a three compartment cell using a mircoporous counter electrode in both acidic and basic media to determine if the pH difference will have an effect on the reaction chemistry. Tests were performed using Pt, $Pt_{.50}$-$Cr_{.50}$, and $Pt_{.87}$-$Ru_{.13}$ in both 0.5 M acidic (H_2SO_4) and 0.5 M alkaline (KOH) media. With this knowledge we can draw conclusions regarding the oxidation process at given potentials and explore intermediate species that poison the catalyst surface. In this work, we present some early results on the electro-oxidation of glycerol in acid and alkaline media, followed by some fuel cell experiments.

Poster Session (2)

Organizer: Michael A. Nichols John Carroll University, University Heights, OH
Organizer: Mark J. Waner John Carroll University, University Heights, OH

Session Overview: Poster Topics are in the general areas of: Organic, Materials, Polymer, Inorganic, and Computational Chemistry

175. Asymmetric Allylation Driven by Amide Dendrimer

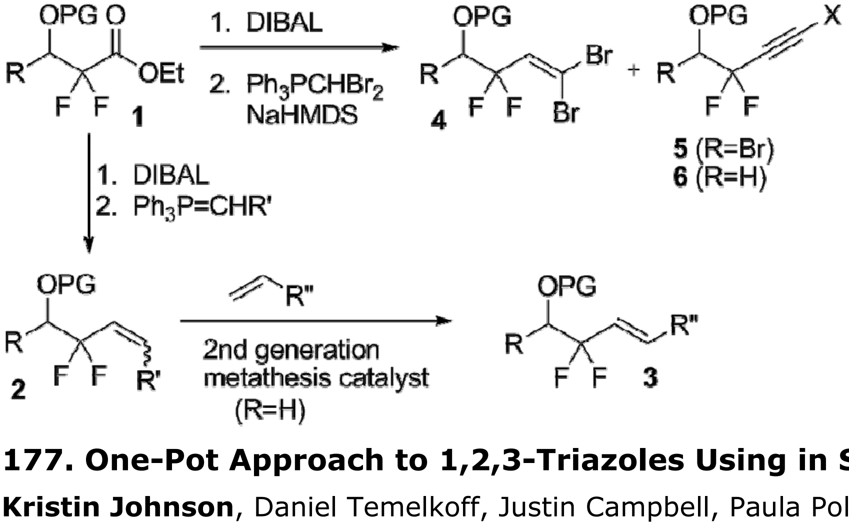
Jianfeng Yu, Christopher G. McDaniel, Siyu Tu, Hui Shao, Chengyang Tie and Jon R. Parquette, Department of Chemistry, The Ohio-State University, Columbus, OH

In the past decade, much interest has been focused on asymmetric catalysis by (R) or (S)- 1,1'-binaphthyl-2,2'-diol (BINOL)-derived chirality titanium (IV) complexes. Several BINOL- titanium (IV) derivatives with substitutes at 3, 3′ positions have been reported. Control of stereoselectivity in the addition reaction of performing allyl stannanes to aldehydes over the titanium (IV) chiral center is one of the interesting. We have designed an amide dendron with two chirality terminal groups, and o-linked coupled the dendron with achiral, racemic bis- or tetraphenolic cores, hoping the hydroxyl groups in the cores can work as a handle to anchor a titanium (IV) and form a catalysis center. Due to the special structure of the dendron, the chiral helical secondary structure can be induced in dendrimers rigidified through intramolecular hydrogen-bonding interactions. So the chiral, nonracemic dendrons o-linked at the achiral, racemic bisphenolic core or tetraphenolic core probability control the helical bias at the periphery of a dendrimer to transfer the chiral information over a longer distance to the achiral center. Comparing the flexibility of bis- and tetraphenolic core dendrimers, we tried explore how to transfer the chirality of terminal groups in the dendron to the catalytic center via dendron secondary structure and how dynamically chiral secondary structure can control the stereoselectivity of a catalytic process.

176. New Approaches to α,α-Difluorinated Alkenes and Alkynes From a Common Difluoro Ester Building Block

Matthew L. Barchok, Alexander J. Seed and Paul Sampson, Department of Chemistry, Kent State University, Kent, OH

Three new approaches for the synthesis of □,□-difluorinated alkenes and alkynes from readily available difluoroester **1** are reported. A Wittig approach affords easy access to □,□-difluorinated alkenes **2** in good yield, albeit with modest Z/E selectivity. A cross metathesis approach has proven successful at creating simple (E)-alkenes **3** but has limited utility for substrates containing non-halo heteroatoms. A Corey-Fuchs approach yields the dibromoalkene **4**, bromoalkyne **5**, and/or terminal alkyne **6** in varying amounts depending on the reaction conditions. Each of these difluoromethylated compounds has promise as a synthetic building block.



177. One-Pot Approach to 1,2,3-Triazoles Using in Situ Generated Azide Anion

Kristin Johnson, Daniel Temelkoff, Justin Campbell, Paula Politis, Krista Cunningham and Peter Norris, Department of Chemistry, Youngstown State University, Youngstown, OH

Alkyl and acyl azides are essential precursors in organic and medicinal chemistry yet they are notoriously difficult to work with because many of them have a habit of detonating when isolated in the pure form. We have developed a new approach to both alkyl and acyl azides, using microwave heating to shorten reaction times, in which reaction progress is monitored by infrared spectroscopy. Being able to follow azide generation *in situ* allows us to track the formation of ionic and covalent azide species conveniently, and then react the alkyl or acyl azide further to produce materials such as 1,2,3-triazoles in one reaction flask with minimal risk.

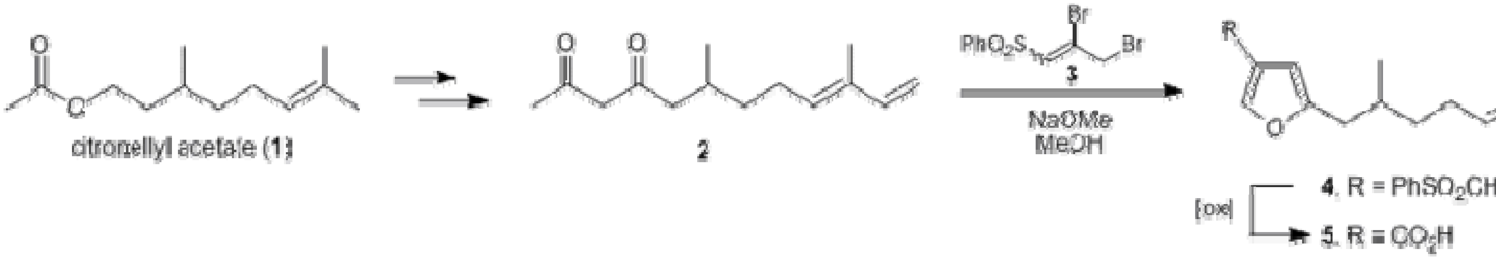
178. An Efficient Synthesis of Nitrogen-Containing Heterocycles Via a Tandem Carbenoid Insertion/Ring-Closing Metathesis Sequence

Oksana Pavlyuk, Henrik Teller, Ross Humes and Mark McMills, Department of Chemistry and Biochemistry, Ohio University, Athens, OH

A series of five- to nine-membered nitrogen-containing heterocycles were prepared via a general and efficient one-pot, two-component sequence featuring rhodium-catalyzed insertion of a vinyl substituted α-diazocarbonyls into the N-H or C-H bond of a series of *tert*-butoxycarbonyl-(Boc)-protected amines, followed by ring-closing metathesis catalyzed by ruthenium benzylidene complexes. This methodology allows easy and convenient access to highly functionalized aza cycloalkenes in good yields in a single transformation.

179. Bioactive Furoic Acids: Total Synthesis of (E)-5-(2,6-Dimethyl-5,7-octadienyl)-3-Furancarboxylic Acid

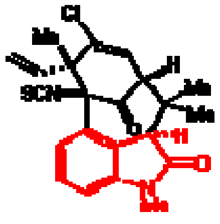
Nicholas S. Duca, Jaimie M. Mong and S. Shaun Murphree, Department of Chemistry, Allegheny College, Meadville, PA



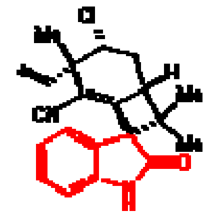
The total synthesis of furoic acid **5**, a marine sponge metabolite exhibiting antifouling properties, is described. The commercially available citronellyl acetate (**1**) is converted to the elaborated β-diketone **2**, which reacts with 2,3-dibromo-1-(phenylsulfonyl)-1-propene (**3**) under basic methanolic conditions to provide phenylsulfonylfuran **4**. The synthesis is completed with a novel oxidative desulfonylation.

180. Chemical and Biological Syntheses of Bioactive Prenylated Oxindole Alkaloids

Rajesh Viswanathan, Case Western Reserve University, Cleveland, OH



welwistatin



welwitindolinone A isonitrile

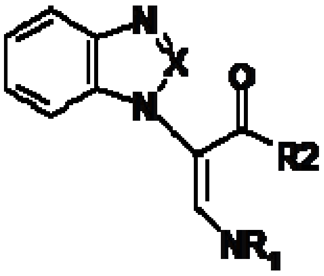
Welwitindolinone C isothiocyanate (welwistatin) belongs to a family of structurally unique reverse-prenylated oxindole alkaloids isolated from the blue-green alga *Hapalosiphon welwitschii*. Several other cyanobacterial sources have been reported to produce these alkaloids: *Hapalosiphon delicatulus*, *Hapalosiphon hibernicus*, *Fischerella ambigua*, *Fischerella muscicola* to name a few. A concise enantioselective approach to the construction of the oxindole portion of the natural product from readily available precursors is presented. The broader scope of this methodology will enable access to other physiologically interesting oxindole motifs present in other natural products such as rhynchophylline and tryprostatins in an enantioselective manner. The biosynthetic pathway leading to this family of alkaloids has not been well studied. Synthetic studies in this direction will aid the preparation of precursors for future biosynthesis studies leading to these oxindole small molecules.

181. Enaminones as Building Blocks in Heterocyclic Synthesis:

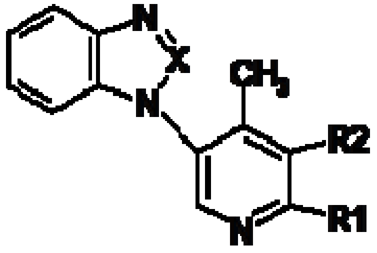
Haider J. Behbehani and Mohammad Elnagdi, Department of Chemistry, Prof. in organic chemistry, Kuwait, Kuwait

Abstract:

The reactivity of enaminoes (1 a-c) toward active methylene reagents and amino-azoles to yield (Compounds 2 and 3) will be demonstrated. A comparison of reaction time and product yields from reactions conducted by conventional heating and by microwave heating will be made. Structure elucidation of reaction products via utility of 2D NMR will also be demonstrated.



1 a-d



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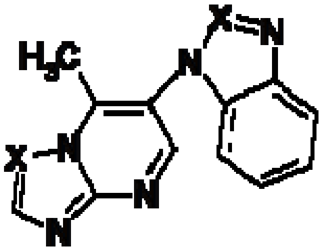


3

1 a, X= N ; $R_1 = R_2 = Me$

b, X= CH ; $R_1 = R_2 = Me$

c, X= N ; $R_1 = R_2 = Ph$

d, X= CH ; R_1 = H ; R_2= Ph

182. Characterization of Anthocyanins In Elderberry (Sambucus Peruviana) Extracts

Liladhar Paudel[1], Faith J. Wyzgoski[2], Sara E. Whitson[3], Peter Rinaldi[4], M. Monica Giusti[2], Nuryati Pangestu[2] and Chrys Wesdemiotis[3], (1)Department of Chemistry, University of akron, Akron, OH, (2)Department of Chemistry, The Ohio State University, Mansfield, OH, (3)Department of Chemistry, The University of Akron, Akron, OH, (4)Department of Chemistry, University of Akron, Akron, OH

Pigments extracted from berries have been found to have pharmaceutical uses in the prevention and/or treatment of diseases caused by retroviruses such as HIV-1 and HIV-2, neoplastic disorders or cancers, and diseases caused by lesions in connective tissues. In our work, the chemical structures of three major pigments in elderberry (Sambucus peruviana) have been elucidated. Two of these components are cyanidin-3-sambubioside and cyanidin-3-glucoside. All the components were separated into three fractions using high performance liquid chromatography (HPLC). Fractions 2 and 3 were identified as cyanidin-3-sambubioside and cyanidin-3-glucoside by HPLC in conjunction with Ultraviolet-Visible (UV-Vis) spectroscopy and Mass spectrometry (MS). The chemical structure of fraction-2 was also verified by nuclear magnetic resonance (NMR) spectroscopy. The structure of the compound present in Fraction-1 has been tentatively identified as a derivative of cyanidin-3-sambubioside with the help of electrospray ionization mass spectrometry (ESI-MS), matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) and NMR spectroscopy. We used both 1D and 2D NMR methods such as total correlation spectroscopy (TOCSY), standard phase sensitive correlation spectroscopy (COSY), double quantum filtered correlation spectroscopy (DQCOSY), heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) 2D NMR to characterize most of the structure components of the compound in fraction-1 of the elderberry extract.

183. NMR Characterization of Poly(lactide-co-glycolide)-b-Polyethylene Glycol)-Folate (PLGA-PEG-FOL)

Linlin Li, Peter L. Rinaldi, Nikki Robishaw and Wiley Youngs, Department of Chemistry, University of Akron, Akron, OH

PLGA-PEG (poly(lactide-co-glycolide)-b–polyethylene glycol), as well as its modified forms, have been widely studied as carriers in biodegradable drug delivery devices. A typical modification form is the introduction of folate at the chain end, which is reported to enhance the targeting ability of the carrier. In our study, both 1D and 2D NMR spectra were collected to characterize the detailed structure of PLGA-PEG-FOL.

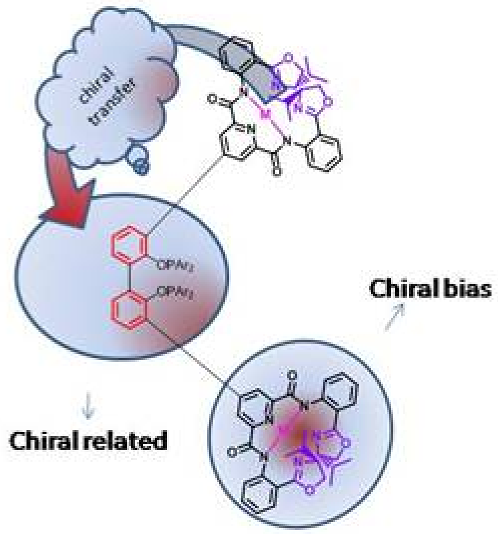
2D-NMR permitted unequivocal assignments of the resonances from the monomer sequence of polymers. The microstructures of different units present in PLGA and PEG and the joints between these two polymer blocks are identified in the 2D NMR spectra. For example, in the PLGA chain, there are different types of monomer sequences including: L-L, L-G, G-L and G-G sequences in the main-chain. In addition, there are a minor number of such sequences at the ends of the PLGA chain.

Once the resonances were assigned based on 2D-NMR data, the corresponding peaks in ^{13}C NMR spectra can be used to assess the composition of the PLGA-PEG-FOL. The ratio of lactate and glycolate units was obtained from the integrals of respective peaks in quantitative ^{13}C NMR spectrum. Furthermore, the number-average lengths of lactate and glycolate sequences in this copolymer were estimated. Thus, we were able to learn whether similar monomer units cluster in a block or if they are randomly distributed in the long chain. Similarly, both qualitative and quantitative studies were performed on the different ethylene glycol units that were present in PLGA-PEG-FOL.

184. Metallodendron Catalyzed Allylic Alkylation

Siyu Tu, Jianfeng Yu, Hui Shao, Chenyang Tie, T.V. RajanBabu and Jon R. Parquette, Department of Chemistry, The Ohio-State University, Columbus, OH

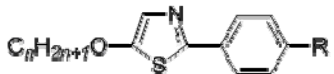
Transition metal catalyzed asymmetric reactions could be reached by efficient and reliable amplification of chirality from chiral ligands which will be more attractive and popular if realized by transferring and propagation of "chiral ligands" whose chirality is induced from dynamic helical bias. Biphenyl phosphine ligands bearing chiral dendrons are used to the allylic alkylation reaction involving Pd catalyst. The initial results by mono-dendron hit 24%ee when isopropyl oxazoline is employed as terminal chiral source at room temperature in THF with as low as 2% catalyst loading. This could be modified by solvent change, temperature lowering, electron density optimization of phosphine center and amplification of chiral information by installing more dendrons. Solvent screen was made and it shows that TBME as non-coordinate solvent gives 30%ee at same condition and other improvements and optimizations are in progress.



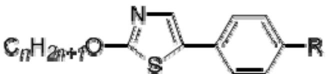
185. Synthesis and Physical Evaluation of 2- and 5-Alkoxy-1,3-Thiazole-Based Liquid Crystals

Alan M. Grubb, Sana Hasan, Andre A. Kiryanov, Paul Sampson and Alexander J. Seed, Department of Chemistry, Kent State University, Kent, OH

Herein we report the synthesis and mesomorphic properties of the first series of 5-alkoxy-and 2-alkoxy-1,3-thiazole-based liquid crystals. The 5-alkoxy mesogens **1** were synthesized through a Lawesson's reagent-mediated cyclization of the corresponding α-benzamido esters, which is not a well explored entry to 5-alkoxythiazoles. The analogous 2-alkoxy-1,3-thiazole-based liquid crystals **2** have been targeted via an S_NAr approach, which has not previously been employed in the synthesis of long chain alkoxythiazoles.



1



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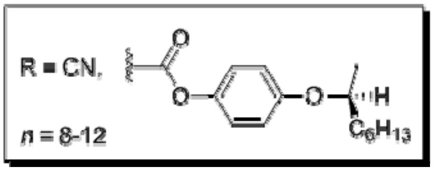


186. Synthesis of Free Base Porphyrin Dendrimers Containing Poly(Glutamic Acid)

Rashid M. Altamimi and David A. Modarelli, Department of Chemistry, The University of Akron, Akron, OH

Dendrimers are highly branched, spherical, three-dimensional polymeric macromolecules that have a large number of terminal groups that control the size, solubility and reactivity of the dendrimer. The aim of this research project is to synthesize three generations (G1-G3) of glutamic acid-based peptide dendrimers having a porphyrin at the core of the dendrimer. The glutamic acid repeat unit used to build the dendrimer branches was chosen to mimic electron-transfer in proteins, through which the mechanism for electron-transfer can be difficult to interpret because of the various possible paths for electron-transfer. We intend to use a combination of steady state fluorescence as well as time-resolved fluorescence, and transient absorption pump probe experiments to measure the electron transfer rate constants in these dendrimers. In this poster, I will present the synthesis of three generations of flexible porphyrin-containing poly(glutamic acid) dendrimers.

187. Syntheses and Characterizations of a Self-Assembled Oligo(phenyleneethynylene)

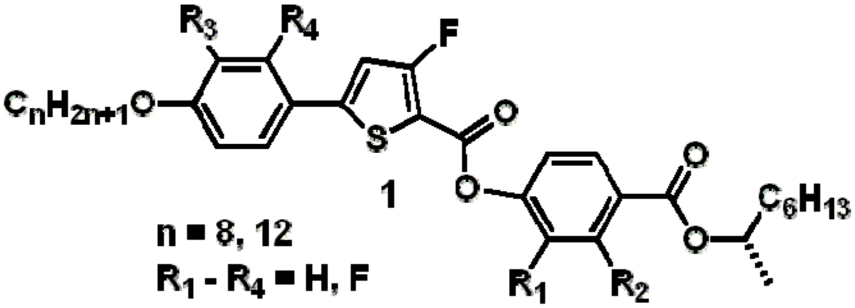
Wongwit Wongwitwichote and David A. Modarelli, Department of Chemistry, University of Akron, Akron, OH

In recent years, π-conjugated macromolecules and self-assembled complexes have attracted the attention of researchers for both their novel properties and as alternative materials to classical semiconductor-based devices. Interchain interactions between π-conjugated molecular wires can potentially influence the electronic and optical performance of organic electronic systems. In this poster, the syntheses, characterization and computational modeling of cross-shaped dimers composed of oligo(phenylene-ethynylene) (OPE) and 3a,6a-bis(diethoxycarbonyl)tetrahydroimidazo-[4,5-d]imidazole-2,5-dione (glycoluril) units are reported. This type of molecular wire can form cross-shaped OPE dimeric complexes by self-assembly, using hydrogen-bonding of the glycoluril units attached to the center of each OPE unit. The results of the photophysical characterization of these self-assembled complexes using UV/Vis and fluorescence spectroscopy will serve as a model for further insight into interchain interactions between OPE units. The results are anticipated to lead to improvements in electronic communication in organic electronic systems that use π-conjugated molecules.

188. Application of 3-Fluorothiophene Building Blocks in Liquid Crystal Synthesis

Pritha Subramanian, Ruth M. Leslie, Andre A. Kiryanov, Paul Sampson and Alexander J. Seed, Department of Chemistry, Kent State University, Kent, OH

This paper will outline the detailed exploration of a Balz-Schiemann approach to 3-fluorothiophenes which has led to the discovery of a convenient gram scale approach to these fluorinated building blocks. The use of these compounds in the synthesis of a family of 3-fluorothiophene-containing liquid crystals **1** will also be presented. Several of these target mesogens possess smectic C phases and may have potential for use in ferroelectric display devices.



1

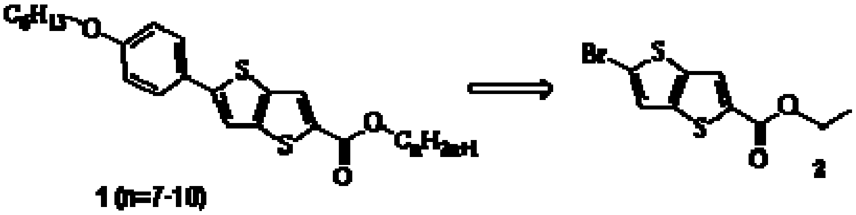
$n = 8, 12$

$R_1 - R_4 = H, F$

189. The Synthesis and Mesomorphic Properties of Novel Thieno[3,2-b]Thiophene-2-Carboxylate Ester Liquid Crystals

Raymond M. Gipson, Alexander J. Seed and Paul Sampson, Department of Chemistry, Kent State University, Kent, OH

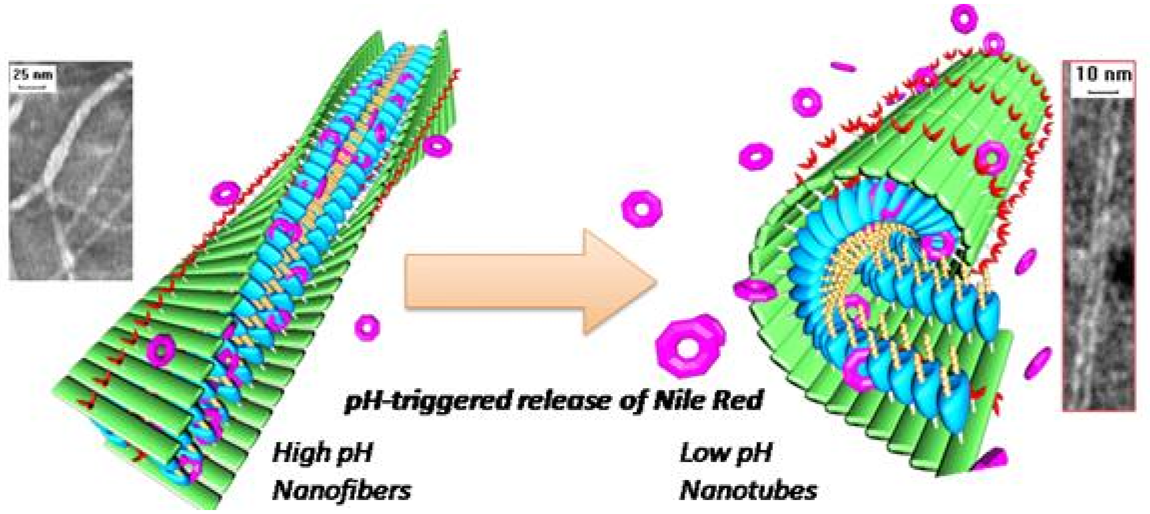
Herein we report the synthesis and mesomorphic properties of a series of alkyl 5-(alkoxyphenyl)thieno[3,2-b]thiophene-2-carboxylate liquid crystals (**1**). Our approach proceeded via the efficient three-step synthesis of ethyl 5-bromothieno[3,2-b]thiophene-2-carboxylate (**2**). Negishi coupling followed by hydrolysis and DCC/DMAP esterification afforded the targeted family of mesogenic esters **1** (n=7-10), all of which exhibited Smectic A phases.



190. Encapsulation of Hydrophobic Molecules by A Self-Assembled Peptide-Dendron Hybrid: Potential Applications in Drug Delivery

Hui Shao, Chenyang Tie, Jianfeng Yu, Siyu Tu and Jon R Parquette, Department of Chemistry, The Ohio State University, Columbus, OH

A peptide-dendron hybrid (**PDH**) , having interdendron spacing of i, i+10 based on an intrinsically alpha-helical, alanine-rich sequence, was shown the capability of self-assembling into either a beta-sheet nanotube or an amyloid-like fibrillar network . The 6 nm diameter of the **PDH** nanotube is among smallest beta-sheet peptide nanotubes that have been observed. The nanotube assemblies displayed exceptional stability at concentrations as low as 5 μM and at temperatures up to 90 ºC. The interconversion between the fibrillar and nanotube assemblies can be controlled by adjusting the salt concentration or pH. The hydrophobic interfaces created by the assemblies efficiently encapsulate hydrophobic molecules in water. **PDH** encapsulated up to 16.1 and 7.2 mol % of Nile red (relative to **PDH**) at pH 11 and pH 7.4, respectively. Further, a significant reduction of the loading capacity occurs going from pH 7.4 to 5.5, the critical pH drop that occurs with endocytosis, suggesting potential applications in drug delivery.



191. Confinement of Elastomeric Block Copolymers Via Forced Assembly

Tiffani B. Abernathy, LaShanda Korley, Anne Hiltner and Eric Baer, Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Forced-assembly processing provides a unique opportunity to study the effects of confinement via conventional melt processing co-extrusion techniques. In this research, an elastomeric triblock copolymer was confined via co-extrusion between alternating layers of a glassy material, such as polystyrene (PS). The microlayering process was utilized to produce novel materials with enhanced mechanical properties through selective manipulation of layer thicknesses and volume compositions. It was anticipated that confinement of the self-assembly process of block copolymers (BCP) would drastically affect the mechanical properties that could be achieved within multilayered films. Multilayer films consisting of an elastomeric, block copolymer confined between rigid PS layers were produced with layer thickness ranging from 10 nm to 600 nm. The layer uniformity and integrity of the multilayer systems have been confirmed for 90/10 and 70/30 compositions of the 257 layer system. The bulk morphology of the triblock copolymer being analyzed was confirmed to be a lamellar structure through SAXS and AFM and the initial data for the multilayer films show no preferential alignment of the lamellae in the extrusion direction. Preliminary DMA analysis showed significant suppression of the alpha-transition associated with the ethylene/propylene mid-block in all compositions. The first series of stress/strain data showed an increase in ductility as the Kraton layer thickness decreases with the mode of deformation changing from crazing to shear yielding.

192. Diethyl 2,3-Di(diphenylphophinato)Butanedioate: A Green Precursor to Flame Retardant Oligomers

Katelyn E. Carter, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI and Bob A. Howell, Center for Applications in Polymer Science and Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48859-0001, Mount Pleasant, MI

The need to develop more effective, more environmentally friendly, and cost effective flame retardants for polymeric materials is ever-increasing. This is largely driven by a heightened concern about the potential negative environmental and health effects of organohalogen flame retardants. In general, these materials are resistant to biodegradation and bioaccumulation in the environment. Ideally, replacements should be effective at low levels, affordable, based on a renewable source, and biodegradable in the environment. Tartaric acid (2,3-dihydroxybutanedioic acid) is a renewable by-product of the wine industry. Thus it is readily available at low cost. It may be converted to an alkyl ester and the hydroxyl groups esterified by treatment with diphenylphosphinic chloride to generate a phosphorus-containing monomer which can be used for the preparation of flame retardant oligomers.

193. Melt Processing of All-Polymer Lasers

Hyunmin Song[1], Ken Singer[2], Tomasz Kazmierzcak[1], Juefei Zhou[3], Yeheng Wu[3], Joe Lott[1], Jim Andrews[4], Chris Weder[1], Anne Hiltner[1] and Eric Baer[1], (1)Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, (2)Departement of Physics, Case Western Reserve University, Clevland, OH, (3)Department of Physics, Case Western Reserve University, Cleveland, OH, (4)Department of Physics and Astronomy, Youngstown State University, Youngstown, OH

Polymers are amenable to melt processing with relatively low cost fabrication methods. Their properties can be readily tailored into flexible, high-performance thin-films which are already replacing inorganic semiconductors in photovoltaic cells, transistors, light emitting diodes, lasers and other devices. We report here on the fabrication of optically-pumped, all-polymer, surface-emitting, distributed Bragg reflector (DBR) and distributed feedback (DFB) dye lasers by multilayer co-extrusion. This method which allows the production of multilayer films with hundreds of alternating nanometer-thin layers capitalizes on the melt-processibility of polymers and has produced large areas of high-quality laser films. DFB laser efficiencies as high as 8% and thresholds approaching 800 mJ/cm^2 and DBR laser efficiencies as high as 19% and thresholds approaching 90 mJ/cm^2 have been fabricated. These flexible thin-film devices can be laminated onto diode pump lasers or photonic circuits. Roll-to-roll processing by multilayer coextrusion of active photonic and electronic devices such as wavelength-agile polymer lasers could open new approaches to display, sensing, optical communication, and data storage technologies.

194. Nanolayering Technology for Probing Homogeneous and Heterogeneous Nucleation

Deepak S. Langhe, Anne Hiltner and Eric Baer, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

A novel methodology for the production of dispersions in which the particles are almost exclusively homogeneous nucleated is derived from layer-multiplying coextrusion. Polypropylene (PP) particles were produced by layer breakup of PP and polystyrene (PS) coextruded nanolayer film by heating these assemblies into the melt. The interfacial driven breakup of the 12nm PP layers produces a dispersion of submicron PP particles in a PS matrix. The PP particles from breakup of 12 nm layers crystallize exclusively by homogeneous nucleation at 40 ºC into smectic form with granular morphology. This gave us opportunity to probe the kinetics of homogeneous nucleation.

The homogeneously nucleated particles were further used to investigate the heterogeneous nucleation. Addition of a nucleating agent to the PP layers offers a unique opportunity to study the nature of heterogeneous nucleation. Two specific nucleating agents investigated include Millad (MD) and Quinacridonequinone (QQ). MD is a sorbitol based nucleating agent for alpha form. The concentration dependence of the multiple crystallization exotherms was interpreted in terms of the binary polypropylene-sorbitol phase diagram. We also investigated the morphological features of PP droplets crystallized in different regimes of nucleation and correlated with our X-ray and differential scanning calorimetry results. Another nucleating agent investigated, QQ, which nucleated bulk PP in ß-form was added to nanolayered system. The dual nucleation of QQ was observed in the PP droplets. In addition to regular beta-form, QQ nucleated PP into alpha-form. High resolution atomic force microscopy was used to confirm the morphologies of the PP droplets.

195. Miscibility of Ethylene-Octene Random Copolymer and Ethylene-Octene Olefinic Block Copolymer Blends

D. U. Khariwala[1], H. P. Wang[1], A. Taha[2], G. Marchand[2], A. Hiltner[1] and E. Baer[1], (1)Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, (2)Performance Plastics and Chemicals R&D, The Dow Chemical Company, Freeport, TX

Recent developments in polyolefin synthesis by The Dow Chemical Company enable synthesis of olefinic block copolymers (OBCs) in a direct way. Copolymers synthesized by chain-shuttling technology have a major fraction consisting of crystallizable ethylene-octene blocks with very low comonomer content, alternating with amorphous ethylene-octene blocks with high comonomer content. The miscibility of random ethylene-octene (EO) copolymers with ethylene-octene olefinic block copolymers (OBC) was studied and compared to EO/EO blends. The EO/OBC blends were miscible if the octene content difference was less than 7 mol% and immiscible above 12 mol%. This contrasted EO/EO blends where, blends were miscible if the difference in octene content was less than about 10 mol% and immiscible if the octene content difference was greater than about 13 mol%. Unexpectedly, it was also found that the phase behavior of EO/OBC blends depended on blend composition even for constituent polymers of about the same molecular weight. Significantly more demixing was observed in an OBC-rich blend (EO/OBC 30/70 v/v) than in an OBC-poor blend (EO/OBC 70/30 v/v). The octene content of the OBC soft block was varied in order to investigate the asymmetric behavior. It was found that extraction of low comonomer OBC fractions into the EO rich phase increases the overall octene content difference thereby causing significantly more demixing in the OBC-rich blends (EO/OBC 30/70 v/v).

196. Stability of Poly(propylene oxide)

Mahmoud R. Al-Omari, Department of Chemistry, Central Michigan University, Mount plesant, MI and Bob A. Howell, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI

Poly (propylene oxide) is a commercial polymer with a variety of applications. One of these is as hydraulic fluid. In this application the polymer must display good tolerance to both mechanical and thermal stress; in particular, thermal degradation can significantly alter the properties of the polymeric fluid. The thermal degradation of Poly (propylene oxide) is being examined using a variety of techniques (TGA, pyrolysis GC, preparative pyrolysis). Thermogravimotry (TGA) suggests that it is quite stable at temperatures below 350 oC. At somewhat higher temperatures it dose undergo pyrolytic fragmentation. It has been reported (S.L.Madorsky and S.Straus, J.Polymer, Sci, 1959, 36,183-194) that the major pyrolysis products are acetaldehyde, prpene and acetone.

197. Transoral Patch Development and Kinetic Study of Drug Release in Artificial Saliva

Arpana Acharya, Alexander Kenneth and Riga Alan, Industrial Pharmacy, The University of Toledo, Toledo, OH

The development and characterization of buccal films loaded with lidocaine were the objectives for this study. Lidocaine has analgesic properties and is a poorly water soluble drug. The key limitations to this approach are the balance in hydrophobicity and solubility parameters between the polymer and the drug and the mimicking of appropriate physico-chemical properties in selecting the dissolution media. A transparent, thermoplastic polymer, Polymethylmethacrylate, was dissolved in acetone (50% w/w) and the solution was poured in a Teflon-coated pan using an inverted funnel on top to ensure slow evaporation. Thickness and weight variation of the films, both with and without drug, were evaluated. Thermal analytical techniques such as Differential Scanning Calorimetry and Thermo-Gravimetric Analysis were used to evaluate film reproducibility and homogeneity. The release kinetics of the drug from the film was studied with the help of dissolution study in artificial saliva. The thermo-analytical and microscopic techniques indicated that the drug was successfully loaded and the prepared films were homogeneous and reproducible. The data obtained from the dissolution study was modeled using multiple equations such as Higuchi, first order, zero order and korsemeyer-peppas functions. The release of drug followed the first order reaction which could be concluded from statistical analysis using goodness-of-fit approaches. The approach of using a polymeric carrier in delivering lidocaine via buccal delivery was demonstrated using in-vitro techniques. Future work should evaluate the impact of plasticizer on modifying the rate of drug release from these polymer films.

198. Enhanced Gas Barrier From Confined Crystallization of PEO In Nanolayered Films

Haopeng Wang[1], Jong K. Keum[1], Chuanyar Lai[1], Benny Freeman[2], Anne Hiltner[1] and Eric Baer[1], (1)Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, (2)Department of Chemical Engineering, University of Texas at Austin, Austin, TX

When polyethylene oxide (PEO) is confined in nanolayer assemblies, it crystallizes as single lamellae, resembling very large, single crystals. The impermeable crystals impart two orders of magnitude reduction in PEO gas permeability. The nanolayer polymer assembly, consisting of thousands of alternating PEO and ethylene-co-acrylic acid (EAA) nanolayers, was achieved by the innovative layer-multiplying coextrusion or "forced assembly". Direct observation by atomic force microscopy, complemented with wide and small angle X-ray scattering, revealed that when the PEO layer thickness was in the micron scale (1-4mm), the PEO lamellar crystal orientation was isotropic. As a result, the gas barrier of PEO layer matched the non-layered PEO control film. The layer confinement effect was progressively shown upon decreasing the PEO layer thickness to around 100nm. The long PEO lamellar crystals were observed to be stacked between EAA layer confinements and were aligned parallel to the layer direction. When the thickness confinement occurred on the 20 nm size scale, the PEO layers crystallize as single, high aspect ratio lamellae that resemble large, impermeable single crystals. The unique PEO crystalline structure imparted two orders of magnitude reduction in oxygen and carbon dioxide permeability. This was attributed to the dramatic increase in the gas diffusion tortuosity in the PEO layer as reflected by the low gas diffusion coefficient in the nanolayered films. Compared with the nano-confinement achieved by self-assembly of block copolymers, the facile "forced assembly" process offers the potential of making high barrier films from conventional polymeric materials.

199. Hierarchically Designed Segmented Polyurethanes for High Performance Applications

J. Casey Johnson and LaShanda Korley, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Nature has proven to be an expert engineer when designing materials that are capable of withstanding complex environments, while still maintaining their mechanical properties, such as toughness, strength and extensibility. The key design component employed is a hierarchical structure that, under deformation or stress, can utilize these multiple levels of organization to absorb energy and reinforce the material such that it will not fail. One of the best known hierarchically structured and strongest naturally engineered materials, spider silk, is composed extensively of beta-sheets that stack into highly crystalline regions which are surrounded by amorphous domains. It is the interaction between the hard crystalline domains and the elastic amorphous domains that give spider silk its strength and toughness. Based on natural materials that self-assemble into hierarchical structures with incredible mechanical properties, we propose to utilize these concepts to design and explore the role of hierarchical ordering in segmented polyurethanes with enhanced mechanical properties. These multi-block polymers consist of a flexible soft segment and a rigid hard segment. The flexible segments form the continuous domain, which is anchored by physical crosslinking of the hard segment aggregates. However, in our system we will incorporate an additional segment, a liquid crystal segment, which should add additional anchoring points as well as deformable/reformable ordering. We have chosen to use polyurethanes due to their dynamic frame work that will allow many adjustable routes, namely the ability to chemically modify the constituents of the hard, soft and LC domains, to achieve maximal mechanical strength and toughness.

200. Characterization of Conjugated Polymer-Semiconductor Nanoparticles Composites

Bimala Lama and Matthew, P. Espe, Department of Chemistry, University of akron, Akron, OH

Characterization of Conjugated Polymer-Semiconductor Nanoparticles Composites

Hybrid photovoltaic devices consist of a conjugated polymer acting as an electron donor and an inorganic material acting as the electron acceptor, commonly semiconductors. In this work, a water soluble conjugated polymer has been combined with CdS nanoparticles that are passivated with thioglycerol. The optical properties of the polymer, nanoparticles and composite have been measured and those for the nanoparticles are unchanged in the presence of the polymer. The polymer, thioglycerol and nanoparticles are being characterized using ^{1}H, ^{113}Cd and ^{13}C solid state NMR to determine the structure of each component in the bulk and at the interface. The ^{13}C SSNMR studies have shown that the morphology of the conjugated polymer at the interface is modified upon interaction with the thioglycerol.

201. Syntheses and Characterization of a Series of Bis-Bidentate Ligands Utilizing 4,4'-Methylenedianiline

Jennifer Kubert, Meghann Mouyianis, Natalie Datien, Charlotte Hsu and Mark A. Benvenuto, Department of Chemistry & Biochemistry, University of Detroit Mercy, Detroit, MI

A series of six ligands, all incorporating 4,4′-methylene di-aniline and utilizing two further donor atoms provided by a series of functional aldehydes, have been produced and characterized. Each ligand is best described as a bis-bidentate moiety containing four Lewis base atoms. Characterization has been predominantly by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, and by single crystal diffraction when possible. This, as well as indications of their metal binding abilities, will be discussed.

202. Enhancing Toughness in a Crosslinked and Telechelic Supramolecular Polymer System

Nicholas R. Wheeler, Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH

A novel biologically inspired polymeric system is being developed that features two separate modes of interchain association, both photoinitiated covalent crosslinking and telechelic supramolecular moieties. The polymer will have a soft core, featuring ultraviolet (UV) crosslinkable pendant groups, and supramolecular end groups that will associate with one another to create hard domains. Crosslinking will be initialized in discreet banded regions via photomasking and UV irradiation while the system is under strain. When strain is released, it is proposed that the highly crosslinked domains will intermingle with one another during the stress relaxation of the polymer matrix.

Supramolecular interactions at the chain ends will be transient because they associate and dissociate, but the covalent crosslinks will be permanent and, thus, subject to a memory effect. The goal is to achieve unique stress strain behavior as the regions of high crosslink density re-segregate upon subsequent straining. The collaboration of many stress-relief events should result in a material of enhanced toughness, analogous to the muscle protein Titin.

203. ESR Study of Electron Beam Irradiated PE Blends

Ann C. Abraham, Ph. D. [1], Michael A. Czayka[2], Michael R. Fisch, Ph. D.[3] and Dylan Miklacic[1], (1)Chemistry, Kent State University-Ashtabula Campus, Ashtabula, OH, (2)Technology, Kent State University-Ashtabula Campus, Ashtabula, OH, (3)Technology, Kent State University, Kent, OH

Initial and recent (though still preliminary) data on electron beam irradiated polyethylene blends will be presented. Test samples were prepared by melt mixing polyethylene and the additive in a Brabender mixer. Additive loadings were 0, 0.5, 1, 2 and 5%. The blends were formed into strands by passing thru a Melt Flow Index instrument and then cut into approx. 37 mg portions. Duplicate samples were matched by weight and irradiated by passing the samples under the electron beam at 20, 40, 60 or 80 kGy doses. Samples were analyzed by ESR (Electron Spin Resonance) immediately after irradiation, 1 hr., 2 hr., 3 hr., 4 hr., and after varying numbers of days. Higher amounts of radicals were observed at higher levels of radiation. Increased loadings of additives seemed to somewhat suppress the formation of radicals. Radicals were observed to decay over the time of the analysis.

204. Self-Assembly Studies of Metallo-Supramolecular Polymers in Solution

Zheng Li, Justin Kumpfer, Adriane Miller, Alexander M. Jamieson and Stuart J. Rowan, Macromolecular Science and Engineering, Case western reserve university, Cleveland, OH

Metallo-supramolecular polymers utilize the binding ability of various metal ions to form polymers of high molecular weight, and offer a convenient route to obtain organic/inorganic hybrid materials. In this study, 2,6-bis(1′-methylbenzimidazolyl) pyridine (BIP) ligand is used as the binding motif with poly(tetrahydrofuran) as the core of a ditopic macromonomer. The metal ions used are Zn^{2+}, Cu^{2+}, and Cu^{+}, which form coordination bonds to N in the BIP ligand. BIP ligands bind the divalent metal ions in a mole ratio of 2:1 and the monovalent Cu^{+} in a mole ratio of 2:2. Static light scattering is applied to probe the supramolecular assembly process and determine the true molecular weight of these metallo-supramolecular polymers. Solution viscosity measurements allow determination of their molecular dimensions. By combining viscosity and computed molecular weight, the hydrodynamic radius and radius of gyration can be estimated for a specified concentration and composition. A transition between supramolecular polymer and monomeric (or oligomeric) states via switching of the oxidation state of copper can be demonstrated using viscosity measurements.

205. Sustainable Synthesis of Monodispersed Spinel Nano-Ferrites

Babita Baruwati and Rajender S. Varma, Sustainable Technology Division, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH

A sustainable approach for the synthesis of various monodispersed spinel ferrite nanoparticles has been developed that occurs at water-toluene interface under both conventional and microwave hydrothermal conditions. This general synthesis procedure utilizes readily available and inexpensive salts as precursors and the method can be adopted for large scale synthesis of these spinel oxides. The ensuing spherical particles are in the size range 8-10 nm and they retain their morphology even on large scale synthesis. The synthesis and post-synthetic surface functionalization of nanoparticles will be described which renders them water dispersible for various applications including catalysis.

206. Rhombic Nanoporous Monolayers Arising From Low Symmetry Amphiphiles

Seokhoon Ahn, Christine N. Morrison and Adam J. Matzger, Department of Chemistry, University of Michigan, Ann Arbor, MI

Two-dimensional (2D) crystals with void spaces formed at the liquid/solid interface have recently emerged as a new class of supramolecular assemblies with the ability act as hosts for guest molecules. These 2D nanoporous networks have generally been constructed by self-assembly of highly symmetric molecules. Here, highly symmetric 2D nanoporous molecular networks containing rhombic voids are demonstrated to be accessible from low symmetry amphiphilic molecules. The amide amphiphiles overcome the barrier to symmetry generation in the two dimensional crystal through forming an aggregate as a building block and their structures will be discussed in detail by high resolution scanning tunneling microscopy (STM) images and computation. This investigation

demonstrates that a high symmetry pattern is achievable without correlation with molecular symmetry through the proper combination of non-covalent interactions of simple amphiphilic molecules.

207. Effect of Acid Concentration On Adsorption Properties of Mesoporous Alumina

Stacy M. Morris and Mietek Jaroniec, Department of Chemistry, Kent State University, Kent, OH

Aluminum oxide synthesis was performed via co-condensation and evaporation induced self-assembly of aluminum alkoxides in the presence of triblock copolymer in ethanol. The concentration of nitric acid, used for hydrolysis of alkoxide, and triblock copolymer, used as a structure directing agent, was altered systematically and the resulting materials were studied in detail. Structural properties such as pore uniformity, pore width, and specific surface area were evaluated from nitrogen adsorption isotherms. The resulting samples featured ordered mesoporosity, relatively high specific surface area, large pore widths and crystalline pore walls. This study represents an efficient and systematic approach to the synthesis and characterization of aluminum oxides with favorable characteristics suitable for catalytic and adsorption applications.

208. Soft-Templating Synthesis and Properties of Mesoporous Carbons and Silicas with Incorporated Nickel Nanoparticles

Laura Sterk, **Joanna Gorka** and Mietek Jaroniec, Department of Chemistry, Kent State University, Kent, OH

Soft-templating strategy used for the synthesis of mesoporous carbons can be easily adapted for organic-inorganic nanocomposites and/or introduction of inorganic nanoparticles into carbon mesostructures. Here this strategy was employed to obtain the phenolic resin-based mesoporous carbons with two different loadings of nickel nanoparticles. Also, this approach was used to obtain nickel-containing mesoporous carbon-silica hybrids, which after dissolving silica with NaOH gave mesoporous carbons with Ni particles and after burning off carbon gave NiO-containing mesoporous silicas. Nitrogen adsorption, low and wide angle X-ray diffraction, transmission electron microscopy and thermogravimetric analysis showed good adsorption and structural properties of the aforementioned materials. Moreover, the use of tetraethyl orthosilicate as an additional pore generating agent afforded Ni-containing micro- and mesoporous carbons with high BET surface areas (~1700 m^2/g). Also, the presence of uniform mesopores with microporous pore walls makes these materials promising for catalysis and related applications.

209. Epoxy/Clay Aerogel Composite Systems

Mohammed Albiloushi, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Mechanical properties and structures were studied for two different epoxy/clay aerogel systems and two different experimental procedures. These aerogels were made using a polymer, two curing agents and clay. The polymer used was 1,4-butanediol diglycidyl ether (BDGE). The curing agents were triethylenetetramine (TETA) and diaminopyridine (DAP). The clay used was sodium-montmorillonite (Na-MMT). Two different mixing methods were used; first was mixing BDGE, TETA/DAP and Na-MMT all together in an electric blender, and the second was mixing BDGE and TETA/DAP and then adding Na-MMT using hand mixter.

In the first experimental procedure, two sets of samples were obtained; set I-A contained BDGE, TETA and Na-MMT, while set I-B contained BDGE, DAP and Na-MMT. For the second experimental procedure, similar sets were obtained but for different mixing method (set II-A and set II-B). Four batches were prepared for each one of the four sets; batches with 5%, 10%, 15% and 20% BDGE. In all batches Na-MMT amount was 5%.

The compressive properties of these polymer/clay aerogel composites of set I-A exceed those of set II-A. However, the mechanical properties and structures of set II-A and set II-B was better than set I-A and set I-B, respectively.

210. Electrochemical Deposition and Post-Processing Treatment of CdTe/CdS Nanowires in Porous Anodic Alumina Templates

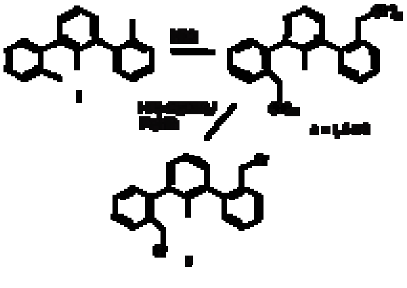
Bo He, Stefan Kraus, Matthias Hanauer and Terry P. Bigioni, Department of Chemistry, University of Toledo, Toledo, OH

Semiconductor CdTe, CdS, and CdTe/CdS nanowires (NWs) were fabricated in porous anodic alumina templates by electrochemical deposition. Thin film post-processing treatments including annealing, $CdCl_2$ treatment, and O_2 treatment were investigated for the NWs to obtain single crystal NWs, to improve the NWs' properties, and to change the quality of the interfaces between CdTe and CdS. The structures and morphologies of the as-deposited and post-treatment NWs have been characterized by optical microscopy, X-ray diffraction, field emission scanning microscopy, transmission electron microscopy, and high-resolution scanning transmission electron microscopy. Energy-dispersive X-ray spectroscopy analysis showed that the CdTe NWs composition is stoichiometric.

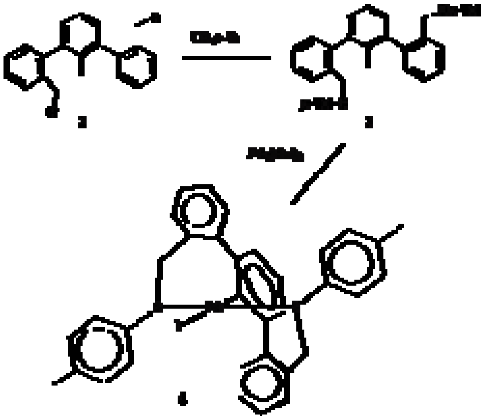
211. Improved Synthesis of Pincer Ligand Precursor, and Synthesis and Structural Characterization of Terphenyl Scaffolded S-C-S Palladium Pincer Complexes

Paul R. Challen[1], Man Lung Kwan[1], John D. Protasiewicz[2], Thomas Spilker[1], Wilson Luu[1], Andrew Schafer[1], Adam Jenkins[1], Laura Gruber[1] and David Essi IV[1], (1)Department of Chemistry, John Carroll University, University Heights, OH, (2)Department of Chemistry, Case Western Reserve University, Cleveland, OH

An easier and more expedient synthesis of 2,6-$(BrCH_2C_6H_4)_2$-4-I-C_6H_3 (**2**) is reported. This material allowed easy synthesis of the new pincer ligand precursor 2,6-(p-tolyl$SCH_2C_6H_4)_2$-4-I-C_6H_3 (**3**) in 87% yield. Compound **3** reacts with $Pd_2(dba)_3$ to give the new palladium pincer complex **4**. Compound **4** has been fully characterized, including structural characterization by single crystal X-ray diffraction methods. The results of the crystallographic work on **4** reveal a twisted type pincer complex not unlike related terphenyl pincer complexes.



Scheme 1. New synthesis of **2**.



Scheme 3. Synthesis of **3** and **4**.

212. Using Collision-Induced-Dissociation Mass Spectrometry to Predict Solution-Phase Relative Affinities of Unidentate Ligands for a Pd(II) Pincer Cation

Norris W. Hoffman[1], Alexandra C. Stenson[1], Richard E. Sykora[1], Rachel K. Traylor[1], Benjamin F. Wicker[1], Samantha Riley[1], David A. Dixon, Dr. [2], Alan G. Marshall[3], Man L. Kwan[4] and Paul Schroder[4], (1)Department of Chemistry, University of South Alabama, Mobile, AL, (2)Department of Chemistry, The University of Alabama, Tuscaloosa, AL, (3)National High Magnetic Field Laboratory, Ion Cyclotron Resonance Program, Tallahassee, FL, (4)Department of Chemistry, John Carroll University, University Heights, OH

Equilibrium constants for $\{Pd_F\}(L)^+ + L^* = \{Pd_F\}(L^*)^+ + L$, where $\{Pd_F\}(L)^+$ is a square-planar fluoroarylbis(phosphinite)palladium(II) pincer, determined in $CDCl_3$ at 23 °C by ^{19}F and ^{31}P NMR were examined for correlation with mass-spectrometric activation-energy parameters for gas-phase Pd-L bond-breaking created by collision with He atoms (CID). Integrals from ^{19}F and ^{31}P spectra of the same mixtures afforded equilibrium constants identical within instrumental uncertainty ($\leq$ 3%). ΔG_{soln} values reflected expected organometallic stereoelectronic trends. Dissociation rate constants k_d for CID of Pd-L were determined from first-order plots against collision time. A parameter mimicking Arrhenius-plot relative activation energy was obtained as the negative slope ($E_{act\text{-}R}$) of a plot of ln k_d versus inverse collision energy. Correlation between $E_{act\text{-}R}$ and ΔG_{soln} was moderately good for a diverse set of P, N, As, Sb, S, and C ligands (R^2=0.67) but better (R^2>0.90) for subsets of similar ligands such as methylpyridines and $P(p\text{-}X\text{-}C_6H_4)_3$.

213. Synthesis and Structural Characterization of Three-Coordinate Manganese, Iron, and Zinc Amido Complexes

Kristin A. Gore and Scott D. Bunge, Department of Chemistry, Kent State University, Kent, OH

Utilizing N,N`-di-alkyl-1,4-diazabuta-1,3-diene ligands, a series of monomeric, low-coordinate metal (M) complexes (M= Zn, Mn, Fe) were isolated and structurally characterized. All syntheses were handled with rigorous exclusion of air and water using standard glove box techniques. Multi-nuclear NMR, infrared spectroscopy, and single crystal x-ray crystallography were used to characterize compounds.

214. Development of Successful Organoplatinum Antitumor Agents

Kelsey N. Stanton and Bob A Howell, Department of Chemistry, Central Michigan University, Mount Pleasant, MI

The serendipitous discovery of the antitumor properties of cis-dichloro(diammine) platinum(II), now known as the drug Cisplatin, a few decades ago ushered in a revolutionary approach to the treatment of cancer. This compound is a broad spectrum, very effective cancer drug. However, its administration is accompanied by a range of side-effects. The two most debilitating are kidney damage and extreme nausea. Many approaches to the reduction of those side-effects have been explored. Thousands of similar compounds in which the amine ligand is varied have been prepared and tested for antitumor behavior. Compounds in which the labile ligands have been varied have been proposed as well. It has been established that chloride is nearly optimum as a leaving group and the removal of the labile ligands should have a half-life of about one hour at 37^{o}C. Based on this, one other (another may be nearing FDA approval) compound has been developed as a successful commercial drug. This is (1,1-cyclobutanedicarboxylato)diammine platinum(II) or Carboplatin. More recently various attempts to support platinum(II) moieties on water-soluble, biocompatible polymers has been undertaken. Slow release of active platinum species in the extracellular fluid might keep the concentration beneath that required for the generation of significant side-effects. Perhaps, the most interesting of these has been the attachment of forty (1,2-diaminocyclohexane)platinum(II) moieties on the surface of a generation 4.5 PAMAM dendrimer.

215. Use of Group 6 Carbonyl Reagents to Stabilize Siliconium Cations

Joanna M. Beres, Alyison Leigh, Chrys Wesdimiotis and Claire A. Tessier, Department of Chemistry, University of Akron, Akron, OH

Silicononium ions derived from hydrido or halo silanes have been proposed as intermediates in organic synthetic transformations. The reaction of $M(CO)_5HMPA$ (M = Group 6) with Si(IV) fragments in benzene produces similar cationic species that are stabilized by weakly coordinating anions in a liquid clathrate matrix. This general synthesis produces a liquid clathrate through the presence of this weakly coordinating anion $[(CO)_5MXM(CO)_5]^-$ where X is a hydride or halide. This anion's specific geometry seems to be crucial to the formation of the liquid clathrate and therefore to the stabilization of the cations. The increased stability of this liquid clathrate has allowed for characterization by ESI MS in addition to NMR and IR. The generality of this synthesis and the characterization of the compounds will be described.

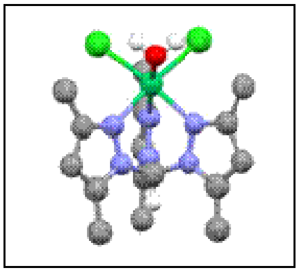
216. Redox-Active Ni(II) Complexes in N3S2 Ligand Fields Inspired by the Nickel-Dependent Superoxide Dismutase

Huaibo Ma[1], Jeffrey L. Petersen[2] and Michael Jensen[1], (1)Department of Chemistry and Biochemistry, Ohio University, Athens, OH, (2)C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV

We recently reported a number of small-molecule nickel(II) complexes featuring both tris(pyrazolyl)borate and heteroatom-substituted dithioacid (O-organoxathate or N,N-diorganodithiocarbamate) chelates (H. Ma, et al. Inorg. Chem. 2008, 47, 7966-7968). This ligand set affords an N3S2 ligand field as a model of the nickel-dependent superoxide dismutase active site (J. Wuerges, et al. Proc. Nat'l Acad. Sci. USA 2004, 101, 8569-8574; D. P. Barondeau, et al. Biochemistry 2004, 43, 8038-8047). This enzyme stabilizes an unusual Ni(III) ion in its resting state, similar to high-valent intermediates invoked in turnover of a number of other nickel-dependent, redox-active enzymes. While our synthetic ligand set affords Ni(II) complexes, we have observed chemical and electrochemical oxidations at low potentials. Recent progress in our ongoing efforts to isolate and characterize the oxidized products will be reported.

217. Oxidative Additions to Ni(0) Supported by a Pseudotetrahedral Enforcer Ligand

Shengwen Liang[1], Swarup Chattopadhyay[1], Jeffrey L. Petersen[2], Victor G. Young[3] and Michael Jensen[1], (1)Department of Chemistry and Biochemistry, Ohio University, Athens, OH, (2)C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV, (3)Chemistry, University of Minnesota, Minneapolis, MN

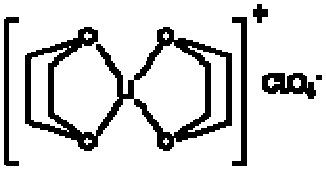


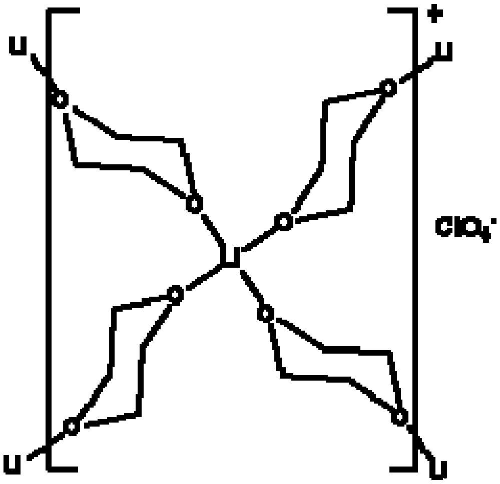
Motivated by oxidative addition reactions proposed at redox-active nickel centers in bacterial metalloenzymes, we are exploring for analogous chemistry at non-classical nickel centers supported by tris(3,5-dimethylpyrazolyl)methane, Tpm*, the neutral analog of the widely exploited tris(pyrazolyl)borate ligand Tp*. We first obtained and characterized a half-sandwich complex Tpm*Ni(OH_2)Cl_2 (pictured at left) by the addition of the free ligand to $NiCl_2$. More recently, a Ni(0) synthon was obtained by addition to Ni(1,4-cyclooctadiene), which readily undergoes oxidative addition reactions with alkyl halides, acyl halides, and peroxyacids. Characterization of the various novel products will be reported.

218. Solvation of Lithium Ion in Polar Aprotic Solvents: Interaction of Lithium Ion with 1,4-Dioxane

David W. Johnson and Amanda Joseph, Department of Chemistry, Universiy of Dayton, Dayton, OH

Anhydrous lithium perchlorate and lithium hexafluoroarsenate react with 1,4-dioxane at 60°C to form a solid solvate. The complexes have the molecular formulas of Li(1,4-dioxane)$_2$$ClO_4$ and Li(1,4-dioxane)$_2$$AsF_6$ respectively. The complex is a white crystalline solid that is sensitive to moisture. The complex has been characterized by infrared and Raman spectroscopy to indicate structure. Infrared and Raman spectra show significant shifts from both 1,4-dioxane and lithium perchlorate. While the 1,4-dioxane has the ability to act as a bidentate ligand to form a strained monomeric complex, the melting points of the complexe are more consistent with a polymeric complex with the 1,4-dioxane ligands acting as bridging ligands.





Molecular orbital calculations are used to estimate the energy difference between the monomeric complex and the polymeric complex. The molecular orbital calculations predict spectra in agreement with the experimentally determined spectra.

219. Synthesis, Spectroscopic Characterization, and X-Ray Structure of a New Five-Coordinated Chlorocopper(II) Complex with a Fluorigenic Ligand

Catherine Miller, Kimberly E. Kern and Michael A. Nichols, Department of Chemistry, John Carroll University, Cleveland, OH

A new copper ion (II) fluorigenic reagent, 8-[(2-pyridine)-methylideneamino] quinoline (PMAQ) was synthesized to be used in a fluorescence quenching study. Following a published procedure, and several modifications, a new Cu-PMAQ-chloro complex was purified and yielded green crystals of the copper complex. After optimum conditions were determined for the synthesis and purification of the Cu-PMAQ complex, the stoichiometry of the complex was revealed from an X-ray structure. The complex was determined to be paramagnetic using EPR spectroscopy. Preliminary analysis using Density Functional Theory suggests that the copper complex is in a trigonal bypyramidal geometry and was optimized without any symmetry restrictions in the doublet state.

220. Synthesis and Characterization of a Novel Multi-Dentate Ligand Incorporating Tris-(2-aminoethylene)-Amine, and Its Metal Complexes

Malinda Killu, Natalie Datien and Mark A. Benvenuto, Department of Chemistry & Biochemistry, University of Detroit Mercy, Detroit, MI

A novel ligand, incorporating tris-(2-aminoethylene)-amine and an aromatic aldehyde has been produced via Schiff's base condensation, and has been characterized. The ligand has the potential to be both hexa- or hepta-dentate. Characterization has been predominantly by ^1H and ^{13}C nuclear magnetic resonance spectroscopy. This, as well as indications of its metal binding abilities, will be discussed.

221. Synthesis, Characterization, and Redox Behavior of Low-Coordinate Phosphorus Compounds

Marlena P. Washington, Vittal Babu Gudimetla, Feng Li Laughlin and John D. Protasiewicz, Department of Chemistry, Case Western Reserve University, Cleveland, OH

The synthesis, characterization, spectroscopic, and redox properties of new low-coordinate phosphorus compounds have been explored. New phosphaalkenes (ArP=C(H)Ar') featuring electron withdrawing/electron donating groups in the para position and phosphorus-carbon heterocyclic compounds have been synthesized and characterized using nuclear magnetic resonance, UV-Vis, and fluorescence spectroscopies. The redox behavior of these new compounds has been investigated using cyclic voltammetry.

222. Group V Metal Complexes of Mono-Anionic Bidentate Acetophenone Imine Ligands

Abdollah Neshat and Joseph A. R Schmidt, Chemistry, The University of Toledo, Toledo, OH

The first step in developing organometallic catalysts is to find a proper ligand system that can easily tune a metal center's environment for specific catalytic purposes. As a ligand system, we are working on acetophenone imine type ligands, and we have developed one-pot, high-yield synthetic routes for their production. As bidentate ligands, their steric and electronic properties can be readily tuned by changing the imine substituents, making these compounds a suitable choice for exploration as new ligands for early metals.

Late transition metal chemistry of these ligands has been explored to a large extent. In contrast, due to the high Lewis acidity of early transition metals and the difficulty of direct metallation of these ligands, reports regarding the use of these ligands with early transition metals are quite limited. Recently, a series of niobium and tantalum imido complexes with mono-anionic orthometallated acetophenone imine ligands have been prepared and characterized using NMR spectroscopy, mass spectrometry and elemental analysis. These low symmetry complexes are produced with only one or two isomers in all cases and display interesting correlations between the steric bulk of the ligands employed and the isomers isolated. Crystal structures and ^1H NMR spectra of several new niobium and tantalum complexes are presented as confirmation of the structural isomers produced.

223. Lithium Adsorption On Graphene Nanoribbons

Chananate Uthaisar, Veronica Barone and Juan E. Peralta, Department of Physics, Central Michigan University, Mount Pleasant, MI

The lithium storage properties of graphene nanoribbons are important for the potential development of rechargeable lithium batteries and hydrogen storage materials. To understand the adsorption of Li atoms at the hollow sites of graphene nanoribbons including zigzag and armachair edges, we performed density functional theory calculations. We found that the binding strength between Li atoms and zigzag nanoribbons is much stronger in comparison with two-dimensional graphene, fullerene or armchair nanoribbons. While the charge transfer between the Li adatom and the zigzag nanoribbon significantly affects the magnetic properties of the latter providing an additional interaction mechanism that is not present in two-dimensional graphene or armchair nanoribbons, we find that the morphology of the edges, rather than magnetism, is responsible for the enhanced Li-nanoribbon interaction. Moreover, we have studied the possibility of higher lithium storage capacity in zigzag nanoribbons. Up to eight Li atoms can be placed into this 32 carbon with 4 hydrogen unit cell where Li:C ratio is 1:4.

224. Preparation of Metal Sulfides and Nanoparticles for Aerospace Applications

J.E. Cowen[1], A.F. Hepp[2], N.V. Duffy[3], M.J. Baird[4], James R. Gaier[2], M.J. Kulis[5], S.A. Duraj[6] and J.N. Williams[6], (1)Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH, (2)Space Processing and Experiments Division, NASA Glenn Research Center, Cleveland, OH, (3)Department of Chemistry, Wheeling Jesuit University, Wheeling, WV, (4)Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA, (5)Space Processing and Experiments Division, The NCSER at NASA Glenn Research Center, Cleveland, PA, (6)Department of Chemistry, Cleveland State University, Cleveland, OH

We describe several related studies where simple iron, nickel, and cobalt complexes were prepared, decomposed, and characterized for aeronautics (Fischer-Tropsch catalysts) and space (high-fidelity lunar regolith simulant additives) applications. We describe the synthesis and decomposition of several new nickel dithiocarbamate complexes. Decomposition resulted in a somewhat complicated product mix with NiS predominating. The thermogravimetric analysis of fifteen tris(diorganodithiocarbamato)iron(III) has been investigated. Each undergoes substantial mass loss upon pyrolysis in a nitrogen atmosphere between 195° and 370°C, with major mass losses occurring between 279° and 324°C. Steric repulsion between organic substituents generally decreased the decomposition temperature. The product of the pyrolysis was not well defined, but usually consistent with being either FeS or Fe_2S_3 or a combination of these. Iron nanoparticles were grown in a silica matrix with a long-term goal of introducing native iron into a commercial lunar dust simulant in order to more closely simulate actual lunar regolith. This was also one goal of the iron and nickel sulfide studies. Finally, cobalt nanoparticle synthesis is being studied in order to develop alternatives to crude processing of cobalt salts with ceramic supports for Fischer-Tropsch synthesis.

225. Cu, in, and Ga Dithiocarbamate Precursors for Thin-Film Solar Cell Materials

S.A. Duraj[1], N.V. Duffy[2], A.F. Hepp[3], J.E. Cowen[4], M.D. Hoops[2], M.F. Baird[2], Jerry D. Harris[5] and M.H.-C. Jin[6], (1)Department of Chemistry, Cleveland State University, Cleveland, OH, (2)Department of Chemistry, Wheeling Jesuit University, Wheeling, WV, (3)BioScience and Technology Branch, NASA Glenn Research Center, Cleveland, OH, (4)Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH, (5)Department of Chemistry, Northwest Nazarene University, Nampa, ID, (6)Materials Science and Engineering, University of Texas at Arlington, Arlington, TX

Ten dithiocarbamate complexes of indium(III) and gallium(III) have been prepared and characterized by elemental analysis, infrared spectra and melting point. Each complex was decomposed thermally and its decomposition products separated and identified with the combination

of gas chromatography/mass spectrometry. Their potential utility as photovoltaic materials precursors was assessed. Bis(dibenzyldithiocarbamato)- and bis(diethyldithiocarbamato)copper(II) have also been examined for their suitability as precursors for copper sulfides for the fabrication of photovoltaic materials. Each complex was decomposed thermally and the products analyzed by GC/MS, TGA and FTIR. The dibenzyl derivative complex decomposed at a lower temperature (225-320°C) to yield CuS as the product. The diethyl derivative complex decomposed at a higher temperature (260-325°C) to yield Cu_2S. No Cu containing fragments were noted in the mass spectra. Unusual recombination fragments were observed in the mass spectra of the diethyl derivative. Tris(bis(phenylmethyl)carbamodithioato-S,S'), commonly referred to as tris(N,N-dibenzyldithiocarbamato)indium(III) was synthesized and characterized by single crystal X-ray crystallography. The compound crystallizes in the triclinic space group P1(bar) with two molecules per unit cell. The material was further characterized using a novel analytical system that combined thermogravimetric analysis, gas chromatography/mass spectrometry, and Fourier transform infrared (FT-IR) spectroscopy to investigate its potential use as a precursor for the chemical vapor deposition (CVD) of thin film materials for photovoltaic applications. Upon heating, the material thermally decomposes to release CS_2 and benzyl moieties in to the gas phase, resulting in bulk In_2S_3. Preliminary spray CVD experiments indicate that $In(S_2CNBz_2)_3$ decomposed on a Cu substrate reacts to produce stoichiometric $CuInS_2$ films.

226. Metallo-Thiophenes with Novel Electronic and Optical Properties: Photoharvestors in Solar Cells

Yagnaseni Ghosh[1], M. H. Chisholm[1], Yao Liu[2], Brian Alberding[2], Claudia Turro[2] and Dr. Terry L. Gustafson[2], (1)Department of Chemistry, Ohio State University, Columbus, OH, (2)Department of Chemistry, The Ohio State University, Columbus, OH

Incorporation of quadruply bonded dimetal MM units, (MM = Mo_2 , MoW or W_2) into thiophenecarboxylates introduces $M_2\delta$ to the thiophene π conjugation giving rise to novel metallo-organic compounds. These hybrid inorganic-organic compounds exhibit excellent electronic conduction and wide range absorption extending from UV-Visible to the near Infra Red (NIR). Strong emission is also observed in the visible as well as in the NIR. Lifetime determination by femtosecond and nanosecond transient absorption spectroscopy and emission decay measurements reveals the presence of both singlet and triplet excited states, with lifetimes in the picosecond and microsecond range respectively. The singlet excited state is ^{1}MLCT, while the nature of the triplet excited state (^{3}MMδδ* or ^{3}MLCT), is dependent on the metal content of the dinuclear core. Wide range absorption and emission in the compounds make them excellent choices as photoharvestors in solar cells and as NIR emitters in metallo-organic light emitting devices.

227. Extended Porphyrins for Dye-Sensitized-Solar-Cells

Rohit Deshphade, Bo Wang, **Hong Wang**, Lin Jiang, ShouZhong Zou and Lei Kerr, Department of Chemistry and Biochemistry, Miami University, Oxford, OH

Porphyrins fused with aromatic rings are a class of compounds possessing unique set of photophysical, optoelectronic, and physicochemical properties. They have great potentials for the application in dye-sensitized-solar-cells. Currently, the synthetic methodologies to prepare these compounds are very limited and often involve harsh conditions and lengthy synthetic steps. In this work, a series of new benzoporphyrins were prepared using a new methodology discovered recently in our laboratory. These new compounds have been characterized using NMR, MS and UV-Visible spectrophotometry. UV-Visible spectra of these compounds show bathochromic shift of the Soret bands by 20-40nm. Redox potentials of these compounds were measured by cyclic voltammetry. Solar energy conversion efficiencies of DSSCs based on these porphyrins were measured.

228. Dielectric Properties of Biaxially Oriented Micro and Nanolayered Films

Joel M. Carr, M. Mackey, A. Hiltner and E. Baer, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH

Capacitors are vitally important in nearly all electronics and electrical power systems. In electrical systems, capacitors play the role that springs do in mechanical systems. Also, a charged capacitor can discharge all of its energy extremely fast; this unique property is used in defibrillators, and reactive armor. In addition to decreasing the size of a capacitor, there is motivation for increasing the performance and efficiency, which comes in part from the drive towards using alternative energy sources, with electrical storage being one option. Our goal in this work is to develop a capacitor film with high energy density and low loss by combining the effects of microlayering and biaxial orientation. Biaxial orientation is commonly used to orient commodity polymers such as polypropylene (BOPP) in an effort to increase various properties such as gas diffusion and electrical breakdown. Based on the fact that energy density is directly proportional to permittivity and the square of electric field, we have made biaxially oriented microlayered films that contain a polyvinylidene fluoride copolymer (PVDF-HFP Solef 21508) and BOPP (Borclean HC300BF) to exploit both high permittivity of PVDF-HFP and high breakdown strength of BOPP. Many compositions of 32 layer microlayered PP/PVDF-HFP films were extruded spanning the entire spectrum from pure PP to pure PVDF-HFP. The low-field permittivity, tan delta, energy density, and breakdown strength were measured as a function of composition. The energy density of the film with the optimum composition was found to have significant improvement over the energy density of the BOPP control film.

229. Fuel From Salt Tolerant Plants and Algae

Michael J. Kulis, Ph.D., NASA-Glenn, National Center for Space Exploration Research, Cleveland, OH, A.F. Hepp, BioScience and Technology Branch, NASA Glenn Research Center, Cleveland, OH and Bilal Bomani, Ph.D, NASA Glenn Research Center, Cleveland, OH

Research in alternative fuels is necessary now in order to face future challenges brought on by peak oil production as well as mankind's escalating impact on the environment. Our effort focuses on the utilization of algae and halophyte plants as a source for aviation fuel. Salt-tolerant plants and algae that can thrive in a wide range of salinity and have significant lipid content have been successfully grown. Efficient extraction processes have been explored in order to extract lipids that can be used as precursors for synthesis of fuel. Refining procedures such as chlorophyll removal and lipid separation have also been explored. Gas chromatography in tandem with mass spectroscopy is currently being utilized in order to qualitatively determine the individual components of the refined extract. We present current findings of lipid content for different species as well as the same species over a range of growth parameters.

230. First-Principles Density Functional Calculations of Hydrogen Molecule Storage On Lithium-Doped Carbon Compounds

Prabath Wanaguru, Veronica Barone and Peralta Juan, Department of Physics, Central Michigan University, Mount Pleasant, MI

Storage mechanisms of hydrogen molecules became the most critical factor for hydrogen-based energy technologies. Storing hydrogen molecules in a phase between chemisorbed and physisorbed levels are crucial to operate at ambient temperature and pressure. Here we present results based on first-principles density functional theory calculations on the hydrogen storage potential of carbon compounds like C_{60}-fullerene, benzene, and naphthalene. We specifically look into the potential of carbon compounds to bind hydrogen molecules mediated by lithium atoms. In these calculations, we looked for the maximum number of lithium atoms that can be adsorbed into the carbon structure and their stability, most favorable position for the lithium atoms, charge acquired by the lithium atoms, and ability of lithium atoms to attract hydrogen molecules.

231. Electrostatic Potentials On the Surfaces of Model Carbon Nanotubes

Zenaida Peralta-Inga, Ph.D. Chemist[1], Jane S. Murray, Ph. D. Chemist[2], Sylke Boyd, Ph.D. Physics [3], Monica C. Concha, Science[1], Pat Lane, MS. Physics[1] and Peter Politzer, Ph. D. Chemist[2], (1)Department of Chemistry, University of New Orleans, New Orleans, LA, (2)Department of Chemistry, Cleveland State Universitiy, Cleveland, OH, (3)Division of Science and Math, University of Minnesota at Morris, Morris, MN

Since the discovery of carbon nanotubes in 1991, their unique chemical, mechanical, electronic, and optical properties have been widely studied because of a variety of potential applications. To help understand and predict nanotube interactions, we have investigated the electrostatic potentials on the outer and inner surfaces of different carbon, boron/nitrogen and carbon/boron/nitrogen model systems, both open and closed. In this poster we analyze and compare the surface electrostatic potentials for a variety of these tubes, also looking at the effects of different caps and substituents. The surface potentials were characterized in terms of both site-specific and global properties: positive and negative extrema, average values, average deviation, positive and negative variances, and electrostatic balance. The composition and structural features of nanotubes can have significant effects upon their surface potentials. In general, for all-carbon closed systems, the surface potentials are weakly positive on most of the outer and all of the inner surfaces. In contrast, the open carbon tubes with charge-donating hydrogens at the ends are slightly negative on the outer lateral surfaces. The boron/nitrogen tubes show positive and negative patterns in the outer surface associated with the boron and nitrogen atoms, respectively, and have much stronger and more variable surface potentials than do the carbon. A strong potential gradient from positive at one end to negative at the other has been observed computationally for donor-acceptor-substituted (n,0) open carbon nanotube models and also particular closed (n,0) carbon/boron/nitrogen tubes.

232. Local Ionization Energies as a Means of Identifying Reactive Sites On the Surfaces of Model Carbon Nanotubes with and without Stone-Wales Defects

Jane S. Murray[1], Monica Concha[2], T. C. Dinadayalane, Ph.D[3], Jerzy Leszczynski[3] and Peter Politzer[1], (1)Department of Chemistry, Cleveland State Universitiy, Cleveland, OH, (2)Department of Chemistry, University of New Orleans, New Orleans, LA, (3)Department of Chemistry, Jackson State University, Jackson, MS

A useful, yet under-utilized, computational tool for identifying the sites in a molecular system most susceptible to reaction by electrophilic attack is the average local ionization energy I(**r**), computed on the molecular surface. I(**r**) is a local property, introduced in 1990 by Sjoberg `et al`, and can be interpreted as the energy required to remove an electron from a point **r** in the space of a molecule. In this poster, we will define and briefly review some practical uses of the average local ionization energy. We will then focus upon an application in the area of carbon nanotubes, looking first at I(**r**) computed on the surfaces of various single-walled carbon nanotube (SWNT) models. We will then compare the reactivity of carbon atom sites of these defect-free tubes with those of tubes containing Stone-Wales defects. We plan to identify the most reactive carbon atom sites in the defect region of the Stone-Wales defective tube, which is considered to be more reactive than the defect-free tube. A Stone-Wales defect is one of the important defects found in nanotubes and is generated by a 90 degree rotation of a C-C bond. The predictions based on the local ionization energy results will be compared with the reaction energies of the addition reactions of hydrogen and fluorine atoms on the surface of selected SWNT models with and without Stone-Wales defect.

233. Reaction Force Analysis of Polyatomic Bond Dissociation

Jane S. Murray[1], Alejandro Toro-Labbé[2], Soledad Gutiérrez-Oliva[2] and Peter Politzer[3], (1)Department of Chemistry, Cleveland State University, Fairview Park, OH, (2)Department of Chemistry, Pontificia Universidad Católica de Chile, Santiago, Chile, (3)Department of Chemistry, Cleveland State University, Cleveland, OH

Earlier work has shown an interesting feature to be associated with the dissociation of diatomic molecules, when analyzed in terms of the reaction force **F**(**R**), defined classically as the negative

derivative of the potential energy V(**R**) along the reaction coordinate. **F**(**R**) has a negative minimum at the inflection point of V(**R**). It was found – using very accurate diatomic potential energy curves – that the minimum of **F**(**R**) always occurs when V(**R**) has increased by about 27% of the amount needed for complete dissociation. The minimum of **F**(**R**) is where the reaction force constant k(**R**), defined as the second derivative of V(**R**), becomes and remains negative. The significance of this **F**(**R**) minimum is that it marks the point of transition from the structural change of stretching the bond to the electronic changes involved in breaking it.

To test this interpretation, and to assess its applicability to bond dissociation in polyatomic molecules, we have investigated the breaking of single bonds in a series of these. The **F**(**R**) minima were located by progressively stretching the bond and finding the points at which the bond-stretching force constant changes from positive to negative, done in two ways: (1) The molecular geometry was relaxed for each value of the bond length, and (2) the geometry of the remainder of the molecule was held constant. By both procedures, the **F**(**R**) minimum is at essentially the same bond length. Also, the **F**(**R**) minimum usually occurs at approximately the same fraction of the dissociation energy.

234. Vibrational Analysis of Molecular Solids: Analyzing Intra- and Intermolecular Contributions to Eigenmodes

Sylke Boyd, PhD, Division of Science and Mathematics, University of Minnesota-Morris, Morris, MN and Kevin J. Boyd, PhD, Department of Natural Sciences, Central College Iowa, Pella, IA

A method to analyze the vibrational spectrum of a molecular solid as to contributions stemming from lattice modes as well as various intramolecular types of motion is presented. This method is illustrated by application to RDX, in both its ideal crystalline form, as well as structures containing various defects. Fifteen internal degrees of freedom, which include bond, bend and dihedral angle vibrations, as well as molecule center-of-mass rotations and translations are selected. The vibrational eigenmodes are then projected onto those specific motions within the system and the contribution to each eigenmode is quantified. Furthermore, correlations are sought between specific intramolecular degrees of freedom and molecular center-of-mass motions. Such an analysis contributes to understanding of the energy transfer between lattice modes and intramolecular degrees of freedom, which is an important factor in shock processes, for example. In case of RDX, this method indicates several groups of doorway modes, which involve significant lattice components as well as rotations of the nitro groups, and thus can serve in the energy transfer from a shock wave to the initiation of bond breaking in this molecule. The poster will focus on the computational details of the projection of eigenmodes onto specific internal modes of the system, such that this method may be transferred to other types of molecular solids.

235. Exploration of Solution Structure and Thermodynamic Parameters Upon Monte Carlo Simulations

Peter I. Nagy[1], Mugunthu R. Dhananjeyan[2], Paul W. Erhardt[1], Edit Baka[3], Gergely Volgyi[3] and Krisztina Takacs-Novak[3], (1)Center for Drug Design and Development and Department of Medicinal and Biological Chemistry, University of Toledo, Toledo, OH, (2)Center for Drug Design and Development, University of Toledo, Toledo, OH, (3)Department of Pharmaceutical Chemistry, Semmelweis University, Budapest, Hungary

Monte Carlo simulations are an effective means to explore solution structures and thermodynamics. Calculations for isobaric-isothermal (NpT) ensembles provide information about important thermodynamic characteristics such as density, enthalpy, and estimates for the relative solvation Gibbs free energy. The relative solvation Gibbs free energy in combination with ab initio calculations for the internal Gibbs free energy allow theoretical prediction of concentrations of chemical species in equilibria such as conformational and tautomeric transformations.

Using the all-atom OPLS-AA pair-potential, solution structures have been explored at T= 298 K and p = 1 atm for 0.2-2 molar aqueous dioxane solutions and for 1 molar tertiary-butyl alcohol systems in pure water, pure acetonitrile, and in water: acetonitrile mixtures. Structures of models were also analyzed when a fluoroquinolone or a progesterone drug-prototype was dissolved in water-methanol-dioxane-acetonitrile solvents with 20 and 40 v/v% water and nearly equal v/v% for the organic components. The calculated densities compared favorably with our experimental values. Solution structures were characterized by means of solute-solvent radial and pair-energy distribution functions, and on the basis of solute-solute distance distribution functions. Significance of the Ewald summation in accounting for the long-range electrostatic interaction energy was pointed out for systems with finite concentration, in comparison with the cutoff method for infinitely dilute solution models. Relevance of the latter approach is shortly discussed in relation to the calculation of the relative solvation Gibbs free energy.

236. Photodissociation of Co-C Bond in Methyl- and Ethylcobalamin: An Insight From TD-DFT Calculations

Manoj Kumar, Department of Chemistry, University of Louisville, Louisville, KY

The mechanism of Co-C bond photodissociation in methylcobalamin (MeCbl) and ethylcobalamin (EtCbl) has been examined by means of time-dependent density functional theory (TD-DFT). The present contribution extends our recent study (`J. Phys. Chem. B` **2007**, `111`, 2419-2422) where relevant excited states involved in the photolysis of MeCbl have been identified. To obtain reliable structural models the high resolution crystal structure of MeCbl was used as the source of initial coordinates. The `full` MeCbl was simplified by replacing the corrin side chains by H atoms and the resulting geometry was optimized. The model of EtCbl was generated from the simplified structure of MeCbl by replacing methyl group with ethyl. For both models the low-lying singlet and triplet excited states have been computed along the Co-C coordinate at TD-DFT/BP86/6-31G(d) level of theory. These calculations reveal that the photodissociation process is mediated by the repulsive $^3(\sigma_{\text{Co-C}} \rightarrow \sigma^*_{\text{Co-C}})$ triplet state. In both cases the key intermediate involved in Co-C bond photolysis is identified as first excited state (S_1). The S_1 intermediate has mixed character: it can be described as predominantly $d_{\text{Co}} \rightarrow \pi^*_{\text{corrin}}$ metal-to-ligand charge transfer (MLCT) state with contribution from σ bond to corrin charge transfer (SBLCT) where upon electronic excitation the electron density shifts from the axial N_{Im}-Co-C bonding to corrin ligand. The major structural change occurs in the N_{Im}-Co-C moiety, which becomes bent with elongated Co-C bond in S_1 state.

Health Impact of Nanomaterials

Sponsor: Bureau Veritas Northeast Ohio American Industrial Hygiene Association
Organizer: Betty L. Hodgson Science Applications International Corp., Cleveland, OH
Organizer: Luz Jeziorowski NASA-GRC, Cleveland, OH
Presider: Luz Jeziorowski NASA-GRC, Cleveland, OH
Presider: Betty L. Hodgson Science Applications International Corp., Cleveland, OH

Session Overview: Applications for the use of nanoscale materials are on the increase. Many applications that are envisioned for these materials will take advantage of the fact that nanomaterials have different chemical and physical properties than materials at larger scales. While these properties can be used for making lighter, stronger composites, to deliver drugs where they are needed, or to clean contaminated soil and groundwater, the ability to evaluate and control the health risks is not as clear. This symposium focuses on understanding and evaluating the potential risks associated with the manufacture and use of engineered nanomaterials and guidance on managing these risks to better protect the workers and the public.

237. Nanoparticles: Potential Health Consequences to the Pulmonary System

Vincent Castranova, PhD, Chief of the Pathology and Physiology Research Branch, NIOSH Health Effects Laboratory Division, NIOSH, Morgantown, WV

Nanoparticles are structures having one dimension less than 100 nm. Therefore, these nanoparticles have a very high surface to mass ratio. Since a large fraction of the atoms comprising a nanoparticle are on the surface, these structures exhibit physicochemical properties unique from their fine-sized analogues. Such unique properties are being exploited for a wide variety of potential applications in electronics, sensors, structural materials, medical imaging, and targeted drug delivery. Since nanoparticles exhibit such unique properties, it is likely that they also possess unique bioactivity. Therefore, exposure may have adverse health consequences. Issues of health concern are: 1) the high fraction of inhaled nanoparticles which would deposit in the lung, 2) the high rate in which nanoparticles migrate into alveolar tissue, 3) their high toxic potency per mass compared to fine-sized particles of the same composition, and 4) the possibility that inhaled nanoparticles may translocate to systemic sites. Evidence supporting these concerns will be discussed. In addition, the biological effects of pulmonary exposure to single-walled carbon nanotubes will be reviewed.

238. Nanomaterials and Health: Synthesis, Uses, and Exposures In Context

Randy L. Vander Wal, Ph.D., Energy and Mineral Engineering, Penn State University, University Park, PA

At the forefront of particulate health concerns are nanomaterials. This talk will propose some considerations for evaluating nanomaterials and their health effects.

1. Is the material as prepared truly "nano"? For example, even though SWNTs satisfy the accepted definition of being nanoscale in 2-dimensions, in practice and certainly as synthesized, they are highly coalesced into aggregates of micron in size.
2. What distinguishing characteristics apply to the particular nanomaterial? High surface area is a universal hallmark of a nanomaterial. Yet fumed silica with a surface area of > 200 m2/g is rated biologically safe and even used a food additive.
3. What are the synthesis methods? Even if synthesis is conducted within a closed system, subsequent processing steps of harvesting and processing can create far greater exposure risk.
3. Do the current markets and/or applications warrant concern? For example quantum dots contain heavy metals, yet they are a commercial product used in limited quantities for biological imaging.
4. What are the exposure routes and levels likely to be encountered in their manufacture, product development and consumer use of nanomaterial based products? Examples in which the nanomaterial, manufacturing process and product are generally considered safe include nanoclays used in various commercial polymers, TiO2 in sunscreen and carbon black in car tires.

The talk will balance these considerations with those nanomaterials derived accidentally such from stationary power generation or transportation. Generally these sources overwhelm potential nanomaterial exposure, even after decades of study and emission controls. Recent studies have linked soot with asthma, heart arrhythmias and even death.

239. Characterization of Engineered Nanoparticles by Analytical Electron Microscopy

Alan. M. Segrave, Director, Laboratory Services, Bureau Veritas North America, Inc., Kennesaw, GA

The collection and analysis of nanoparticles presents many challenges to the industrial hygienist and analyst in the laboratory. Several collection and analytical techniques for characterizing engineered nanoparticles will be discussed emphasizing the "real world" requests the laboratory receives in the field of nanocharacterization. Special emphasis will be placed on the use of analytical electron microscopy in the characterization of engineered nanoparticles. The presentation will provide useful insight and practical approaches to characterizing nanoparticles.

240. Pulmonary Toxicity of Manufactured Nanoparticles

Brian C. Peebles[1], Amber Nagy[2], Prabir K. Dutta[1] and W. James Waldman[2], (1)Department of Chemistry, The Ohio State University, Columbus, OH, (2)Department of Pathology, The Ohio State University, Columbus, OH

Manufactured nanomaterials have become ubiquitous in science, industry, and medicine. Although electron microscopy and surface probe techniques have improved understanding of the physicochemical properties of nanomaterials, much less is known about what makes nanomaterials toxic. Particulate matter less than 2.5 micrometers in diameter is easily inhaled and taken deep into the lungs. The toxicity of inhaled particulate matter is related to its size and surface chemistry. Permissible exposure limits to micrometer-size particulate matter in the workplace are in place, but current limits do not specifically address the role of surface chemistry and the potentially higher toxicity of nanomaterials. The size, agglomeration characteristics, and surface chemistry of several manufactured nanoparticles including carbon, titania, and aluminosilicates are being studied and manipulated to explore the causes of their toxicity. Inflammatory response and cytotoxicity following exposure of human and murine macrophages to nanoparticles are being employed as indicators of particle toxicity. The results are expected to lead to more effective standards for nanomaterial exposure in the workplace and pathways to toxicity mitigation.

241. Nanomaterials: Worker Protection Programs

Dan Markiewicz, MS, CIH, CSP, CHMM, Markiewicz & Associates Ltd., Toledo, OH

Work with nanomaterials involves some hazards and risks that may not be fully characterized. These uncertainties warrant that employers develop and implement a nanomaterials health and safety program to help protect workers from potential illness or injury. Where an employer already has a comprehensive worker health and safety management system modeled under the elements in the ANSI/AIHA Z10-2005, or equivalent system, then the nanomaterials program may be integrated into it. Where the employer lacks a comprehensive worker health and safety management system, the nanomaterials health and safety program must stand alone. This presentation describes the key elements that should exist in an effective nanomaterials health and safety program.

242. Medical Surveillance for Nanotech-Exposed Workers

Kathleen M. Fagan, MD, MPH, Occupational Safety and Health Administration, Washington, DC, DC

The diversity of both the chemical composition and the properties of nanomaterials makes the prediction of adverse health effects extremely difficult. Research to determine the toxicity of specific nanoparticles has only recently begun. Some studies, such as those comparing the pathologic properties of carbon nanotubes to asbestos fibers, raise significant concerns. Environmental and biological monitoring for exposure to nanomaterials are still in development. With so many questions and so few answers, how can effective medical surveillance be designed to protect workers exposed to nanotech materials? The National Institute of Occupational Health and Safety has recently published "Interim Guidance for Medical Screening and Hazard Surveillance for Workers Potentially Exposed to Engineered Nanoparticles". This NIOSH guidance will be reviewed, and the ethical issues involved in medical screening in the setting of so many unknowns will be discussed.

100 Years of Chemistry in Cleveland

Organizer: Helen Mayer GrafTech, Parma, OH
Presider: Helen Mayer GrafTech, Parma, OH

Session Overview: In 2009, the Cleveland Section is celebrating 100 years of association with the national American Chemical Society. The Cleveland Section is noted for the number of historical events in chemistry that happened here. The section has been honored by six Chemical Historical Landmarks which will be featured in this session.

243. Susan Reeve Lyon and Practices of Seventeenth Century English Apothecaries

A. L. Wilson, Oolong Informatics, Morgantown, WV

Susan and William Reeve were apothecaries in London. After Susan Reeve was widowed, she continued to work as an apothecary with her apprentice. By 1632 she had remarried although her new husband, William Lyon, was described by the College of Physicians of London (CPL) as "no Artist."

After 1618 apothecaries were supposed to use recipes from the *Pharmacopoea Londinensis*, written by the CPL. Susan Lyon would have compounded these remedies to fill prescriptions of English physicians. Good laboratory skills were required. Raw materials were pulverized in a mortar and pestle, and extracted with suitable solvents. Refluxing was used for some medicines. Mistress Lyon would have distilled natural products to make remedies like "Aqua absinthii", "Aqua Buglossi", essential oil of cinnamon and distilled chicken soup. Many lab techniques Susan Lyon used in 1632 are still taught in sophomore organic chemistry labs.

Physicians also prescribed nostrums containing toxic heavy metals. Unfortunately, organometallic compounds were the only effective treatments for French pox (syphilis). These included "Oleum antimonii" and "Mercurius Dulcis". Universities taught Latin and Greek; they did not teach chemistry, toxicology or early modern botany. Women were not permitted to attend universities or become members of the CPL.

Women like Susan Lyon learned to be apothecaries by completing a seven-year apprenticeship. Seventeenth century apothecaries made medicines from raw materials like herbs, spices and animal products. Sometimes they even used metal ores. Apothecaries routinely used many lab skills we still teach in undergraduate chemistry courses.

244. 100 Years of Chemistry in Cleveland

Helen Mayer, GrafTech, Parma, OH

The Cleveland Section of the American Chemical Society is celebrating its 100th anniversary of affiliation with the national American Chemical Society, but the history of chemistry in Cleveland starts long before that. Cleveland has been a center of the development of industrial chemistry throughout its history. Cleveland has been crucial to the development of several industries—petroleum, aluminum, paint, batteries, carbon, and polymers, to name a few. Scientists and engineers working in Cleveland have provided the world with inventions such as the first electric street light, a way to make aluminum, waterborne paint, dry cell and alkaline batteries, carbon fibers for aerospace applications, the first municipal water softening plant, the fluorescent lamp, and iodized salt. An overview of the interconnectivity of Cleveland's six Chemical Historical Landmarks as well as other fun facts about the history of chemistry in Cleveland will be presented.

245. A Revolution in the Everyday Use of Metal; Charles M. Hall's Discovery of the Method for Refining Aluminum by Electrolysis

Norman C. Craig, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH

On February 23, 1886 in the woodshed attached to his family's home in Oberlin, OH, Charles M. Hall discovered the electrolytic process for refining aluminum metal. The discovery, which was dependent on proximity to Cleveland's industry, spawned a new industry and transformed aluminum from being a precious metal with a value comparable to that of silver into an everyday substance. This important discovery was celebrated by the ACS with a Historic Chemical Landmark designation in September 1997. We will review the path to the discovery and commercialization. We will also describe how inexpensive aluminum became an everyday substance and transformed the uses of metals.

246. Edward Williams Morley: “It's 15.879 ± 0.001”

William Fickinger, Department of Physics, Case Western Reserve University, Cleveland, OH

There were very few scientist researchers in the United States in the nineteenth century, and most of these were trained in Europe and then joined faculties of the major universities in the East. Edward Morley, who had no formal training in advanced chemistry, nor any advanced science degree, spent 37 years as professor and independent researcher at Western Reserve University in Ohio. Nevertheless, by 1895 he was president of the AAAS and four years later, president of the American Chemical Society. While his name is most often linked to that of Albert Michelson, his partner in the famous and one-time controversial ether drift experiment of 1887, that work was only incidental to his major contributions to physical chemistry.

This paper is concerned with Morley’s precision measurements of the ratio of the atomic weight of oxygen to that of hydrogen. Ever since the not unreasonable 1815 proposal by William Prout that all atomic weights should be integral multiples of that of hydrogen, experimenters had begun to question this prediction as laboratory techniques improved. However, it was not until Morley’s publication in 1895 that most were convinced that Prout’s idea was just an approximation.

Morley spent many years perfecting his instrumentation and techniques. He was able to declare that the oxygen to hydrogen ratio was significantly less than 16. His result, good to one part in ten thousand, was 15.879. This presentation will illustrate a description of Morley’s work with original figures from his Smithsonian Institution paper.

247. From the Columbia Battery to the Twenty-First Century

Virginia M. Brandt, Technology, Energizer, Westlake, OH

For 123 years, Energizer has played a vital role in how people throughout the world live, work and communicate. In 2005, the ACS recognized Energizer’s development of the Columbia battery as a seminal contribution to national and, subsequently, international industrial and economic development.

In 1886, Energizer (then called National Carbon Company) marketed the very first portable power source for consumer use: the “Columbia" 1.5-volt dry cell battery. “Columbia,” six inches tall and, with two cells in a lantern, weighting over six pounds, was the world’s first dry cell battery manufactured and distributed on a large scale, meeting the demands of the growing telephone and automobile industries. Thus, Energizer made significant contributions toward the industrial development of the country, and subsequently, the world. By commercializing the Columbia, Energizer created the modern battery industry.

In 1959, Energizer once again revolutionized the industry, introducing alkaline battery technology. Energizer continued its leadership throughout the second half of the twentieth century and into the new millennium: Energizer became the first battery maker in 1990 to eliminate adding mercury to its batteries; and today, Energizer’s technical leadership is evident by continuous improvements in battery life, higher quality of battery power, new packaging and product features and a steady stream of new lighting products.

From the historical Columbia battery to the new Zinc Air Prismatic battery, Energizer proudly continues to provide consumers with innovative, high-quality and technologically advanced batteries and flashlights. We are dedicated to predicting and meeting the needs of consumers all over the world.

248. The Sohio Acrylonitrile Process - A National Historic Chemical Landmark

Mark C. Cesa, Ph. D., Process Technology, INEOS Nitriles, Naperville, IL

On September 13, 1996, the ACS designated the invention and development in Cleveland and Lima, OH, of the Sohio Acrylonitrile Process as a National Historic Chemical Landmark. In the Sohio Acrylonitrile Process, acrylonitrile is manufactured by ammoxidation of propylene, an innovative, single-step catalytic reaction of propylene with ammonia and oxygen over a fluidized-bed mixed metal oxide catalyst. As a result of an intensive research and development effort at The Standard Oil Company (Sohio) in the 1950's, the Sohio process made inexpensive acrylonitrile available to the marketplace and led to rapid growth in applications from plastics and fibers to industrial chemicals. Today nearly all the world's acrylonitrile is produced by the Sohio process. The Sohio Acrylonitrile Process is a model of the discovery of a breakthrough chemical technology and its successful development and commercialization. This talk describes the efforts of a unique group of talented scientists, engineers, and businessmen to bring acrylonitrile technology to reality and to maintain its leadership position in the chemical industry.

249. The Discovery and Development of High Performance Carbon Fibers

John C. F. Chang, GrafTech International Holdings, Inc., Parma, OH

On September 17, 2003, Parma Technical Center of GrafTech International was designated as a National Historic Chemical Landmark, for the development of high performance carbon fibers. Scientists at the Parma Technical Center performed pioneering research on high strength, high modulus carbon fiber materials. In 1958 Roger Bacon demonstrated the ultrahigh strength of graphite in a filamentary form, called graphite whiskers. In making these graphite whiskers, it is thought he may have also produced carbon nanotubes. Seven years later continuously processed high performance carbon fiber, from a rayon precursor, was commercialized. In 1970 Leonard Singer produced truly graphitic fibers, leading to the commercialization of carbon yarn derived from liquid crystalline pitch, or mesophase pitch. These fibers are used in aerospace and sports applications.

Functional Materials: Emulsion Polymers - Materials & Characterization

Sponsor: None
Organizer: Duke Rao Sherwin Williams, N/a, OH
Presider: Madhukar (Duke) Rao, Director The Sherwin Williams Company, Cleveland, OH

Session Overview: The Emulsion Polymers/ Characterization session will cover Various Waterborne Polymer technologies(including various dispersions and hybrids), Surfactant Technologies in Emulsion Polymerizations, and characterizations of these polymers by physical characterization techniques.

250. Surfactants for Emulsion Polymerization

Yi-Zhong Li, Master degree of chemical engineering, Rhodia Inc., Cranbury, NJ

Surfactants are a family of key components in making emulsion polymers. They play critical roles in controlling particle size and providing the necessary stability of the emulsion products.

In this presentation, the fundamental principle of interfacial phenomena, the structural and physical properties of surfactants, and the relationship between functions of surfactants and their structures will be described. A wide variety of surfactant chemistries, their functions, and how to apply them in EP application will be discussed.

251. New High Performance Alkyl Phenol Free Surfactants with Improved Physical Properties

Ana Fernandez, Ph D polymer Science, Functional Products, Cognis Corporation, Ambler, PA

This paper introduces a new generation of alkyl phenol free nonionic surfactants. The new surfactants are environmentally compatible exhibiting effective performance during polymerization and post-polymerization stabilization. These liquid surfactants meet demanding physicochemical properties, regulatory compliance and performance requirements. They exhibit low freezing temperatures, excellent water miscibility, minimum gel phase formation and low viscosity at high solids content. They are clear, high solid liquids at room temperature, the new surfactants are easy to handle and very effective during polymerization providing overall latex stability. The paper focuses on their chemical and physical properties as well as on their performance in model acrylic formulations for architectural coatings.

252. Structural Evolution of Monomer Drops and Polymer Particles in Heterogeneous RAFT Polymerizations

Jennifer O'Donnell[1], Binh T.T. Pham[2], Gregory G. Warr[2] and Brian Hawkett[2], (1)Department of Chemical and Biological Engineering, Iowa State University, Ames, IA, (2)School of Chemistry, The University of Sydney, Sydney, Australia

We have discovered a novel method for directly preparing aqueous dispersions of submicron-sized hollow particles by using an amphiphilic poly[(acrylic acid-co-butyl acrylate)-b-styrene] chain transfer agent as the stabilizer in heterogeneous reversible addition-fragmentation chain transfer (RAFT) polymerizations.[1] This method produces hollow particles in a single processing step with fine control over particle wall thickness. However, undesired particle morphologies, such as elongated hollow particles and solid spherical particles, are often observed. Therefore, insight into the hollow particle formation mechanism in these polymerizations is necessary to improve the control over particle morphology.

Small angle neutron scattering (SANS) is uniquely capable of probing the lengthscales of the monomer drops, the hollow particle shells, and the solid polymer particles in situ without destroying the radical activity. We have used SANS to monitor the structural evolution of the monomer drops and polymer particles during the initial mixing stage and throughout the polymerization. Experiments were performed at several ratios of monomer to chain transfer agent, and sodium hydroxide to acrylic acid, as well as several shear rates. Transmission electron microscopy was used to directly visualize the final particle morphology, and to assist in the analysis of the SANS data. The sodium hydroxide to acrylic acid ratio and the shear rate were found to be the critical parameters for hollow particle formation.

[1] Vesiculated Polymer Particles. Australian Provisional Patent number 12844010, October 2006

253. Recent Advances In Polyurethane Dispersions

Alex Lubnin, Sr. R&D Associate, Lubrizol, Cleveland, OH

Several recent contributions by Lubrizol to the field of polyurethane dispersions (PUDs) will be reviewed:

1. Pre-plasticized PUDs

Use of plasticizers in prepolymer achieves two main goals:

- Eliminates the need for NMP solvent to reduce the process viscosity and dramatically reduces VOC;
- Pushes the limits on softness of polyurethanes and produces super-soft PUDs unattainable by conventional tools.

Other benefits delivered by some specialty plasticizers include biorenewable content, flame retardancy, breathability, reactive crosslinking, hydrophobicity, `etc`.

2. “Breathable” PUDs

Novel class of VOC-free PUDs delivers the levels of MVTR comparable to Gortex® and combines the ease of use of polymer dispersions, outstanding stability to virtually any kind of additives and ability to tune in desired softness or hardness.

3. Inorganic-PUD nano hybrids

New proprietary process produces well exfoliated colloidally stable PUD-inorganic nano hybrids. They deliver nanotechnology to customers in a safe and convenient form. Nanofillers impart useful properties onto polymers without compromising transparency and esthetics of the coatings.

4. Core-shell and structured PUDs

Novel two-prepolymer process for making PUDs is a new tool for introducing and controlling PUD particle morphology. New family of structured PUDs include dispersions with core-shell, asymmetric core-shell and "ice-cream cone" morphologies.

5. Hollow and porous PUDs

The two-prepolymer method for making core-shell PUDs was adapted to make hollow PU particles unattainable by the prepolymer process before.

6. UV-curable RAFT PUDs

Novel functional RAFT agents invented in Lubrizol can be incorporated into the backbone of polyurethanes. They introduce UV sensitive dithioester groups into the backbone of PUDs and trigger UV-initiated polymerization of acrylic monomers in the absence of objectionable UV initiators.

254. Amphoteric Binder System for Waterborne Stain Blocking Primers Suitable for Use at Very Low VOC Levels

Richard Flecksteiner, Alan Fream, Maurille Secher, Sebastien Freal-Saisson, Regina Matranga and Brian Doran, Eliokem Materials and Concepts, Akron, OH

Amphoteric Binder System (ABS) technology has been developed for use in low VOC, waterborne stain blocking primers. The ABS is a small particle size, low T_g, core/shell acrylic copolymer dispersion. The particles contain both anionic and cationic character which leads to its unique properties. Because of the cationic nature of the polymer dispersion primers show excellent stain blocking, especially to hydrophillic stains, which are predominately anionic in nature. The anionic character of the ABS allows for more formulation latitude than is common for cationic resins as well as increasing adhesion to a wide variety of substrates. The use of ABS in a primer will be compared against currently available technology to highlight the advantages of this new technology.

255. Morphological Investigations of Multi-Phase Polymeric Materials

David F. Klimovich, Sr. Scientist, Paint & Coatings Division, Sherwin-Williams Co., Cleveland, OH and Nemi C. Jain, Sr. Scientist & Team Leader, Analytical Sciences, Automotive Division, Sherwin-Williams Co., Warrensville Hts., OH

Many commercially available latex polymers are now multi-phase materials, with each phase having a different composition and usually a different glass transition temperature. Although these latexes tend to be called core/shell polymers, many different morphologies are possible. In this presentation, I will discuss the different latex morphologies that have been observed in the literature, along with techniques that we have used to analyze the morphologies of multi-phase latexes in our labs, and our conclusions as to which type we are seeing. The techniques we use include TEM of latex particles and AFM of films made from the latexes. Samples analyzed include several types of acrylic latex coatings and an emulsified alkyd.

TEM has been used for many years to image multi-phase materials. Sometimes an appropriate staining technique has to be employed to improve contrast, but we have also found that at times staining is not necessary, as we will show. AFM has been found to be very useful in imaging films made from latexes, even after coalescent solvents have been used to produce a coalesced film. The phenomenal z-resolution of the AFM has allowed us to see the remnants of particles in these films, and the compositional contrast obtained from a Tapping Mode image has offered information on the location of the different phases in the polymer.

We have found that TEM and AFM complement each other very well in determining the structures of the latex films we can produce with these polymers, as I will discuss.

256. Characterization of Functional Polymeric Materials for Coating Industry: Classical and Newer Approaches

Nemi C. Jain, Sr. Scientist & Team Leader, Analytical Sciences, Automotive Division, Sherwin-Williams Co., Warrensville Hts., OH

We have been characterizing polymers, polymeric materials and coatings for the last two decades. In the first decade or so, we mainly utilized chromatographic (GC, Pyrolysis GC/MS, GPC and HPLC), spectroscopic (UV/Visible, FT-IR, FT-NMR), microscopic (optical, SEM/X-ray), thermal (DSC) and physical (wet chemistry, contact angle, surface tension, particle size, etc.) methods to characterize reducers, resin binders, dispersions, pigments, additives, and coatings. In recent years we have added several newer methods to our laundry list to dig deeper into the structural aspects of the polymeric materials. For example,

(i) Characterization of polyisocyantes by Fast atom bombardment mass spectroscopy (FAB-MS), (ii) Microscopic studies of Nano polymers by TEM and AFM, (iii) Surface analysis of polymeric films by X-ray photoelectron spectroscopy and laser Ablation ICP-MS, (iv) Characterization of ketimine and epoxy products by GC/MS, LC/MS, and FAB-MS. (v) Kinetic studies of urethane coatings using ATR FT-IR, and (vi) Characterization of polyesters by MALDI-MS.

In this meeting, we will present some of the examples and characterization methods used to solve industrial problems. We will also discuss how the characterizations are crucial to the coating industry in the current global environment.

Organic Chemistry: New Synthetic Methodologies (1)

Sponsor: ACS Division of Organic Chemistry, Quanta BioDesign, Ltd., Toledo Section of the ACS
Organizer: Suri S. Iyer University of Cincinnati, Cincinnati, OH
Organizer: Steven J. Sucheck University of Toledo, Toledo, OH
Presider: Suri S. Iyer University of Cincinnati, Cincinnati, OH

Session Overview: The symposium will broadly feature new synthetic methods and the application of new methods for the preparation of organic compounds. The scope of the symposium will cover topics such as new functional group transformations, green chemistry, asymmetric syntheses, catalytic, metal-mediated, enzyme-mediated reactions and total synthesis of natural and unnatural products. Presiding : Suri S. Iyer, Assistant Professor, 805 Crosley, Department of Chemistry, University of Cincinnati, Cincinnati, OH -45221. Ph: 513-556-9273 Fax: 513-556-9239 Email : suri.iyer@uc.edu http://www.che.uc.edu/iyer/

257. Towards Green Azidation Chemistry

Peter Norris, Department of Chemistry, Youngstown State University, Youngstown, OH

Organic azides play important roles in synthesis, for example as intermediates `en route` to other functional groups and as precursors to various heterocyclic systems. Since low molecular weight azides are potentially explosive when isolated in pure form, there is somewhat of a reluctance to use them, particularly in industry. We have developed a novel method for the synthesis of alkyl and acyl azides that avoids the use of NaN_3 and the isolation of the azide product. Using microwave heating speeds up the formation of our azidation reagent and by using IR spectroscopy we are able to monitor the progress of reactions safely and conveniently. We will discuss this methodology and our progress in applying some of the principles of green chemistry to minimize waste and hazards.

258. High Speed Ball Milling as An Environmentally Friendly Approach to Organic Synthesis

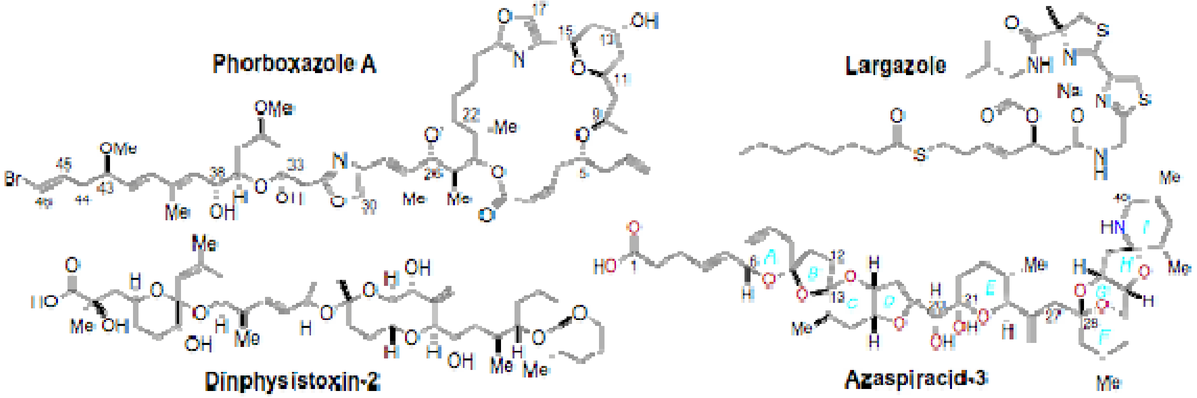
Daniel C. Waddell, Indre Thiel, S. Tyler Marcum, Brandon Smith and James Mack, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Due to increased interest in the development of more environmentally benign synthetic methods, there is a strong effort to revolutionize the manner by which chemists conduct organic reactions. One method is the use of a novel, high energy, solvent-free technique known as high speed ball milling (HSBM). Since conducting chemical reactions under these conditions is a new area, many of the fundamental rules that govern these reactions need to be understood. We report our ability to generate regio- and stereoselective enolates of 2-methyl cyclohexanone. Our results show that we can selectively create kinetic vs thermodynamic products utilizing HSBM. Using sodium hydroxide we observe a thermodynamic: kinetic product ratio of 13.5:1. Alternately, using lithium hexamethyldisilazide we observe thermodynamic:kinetic product ratio of 1:2. We also discovered NaH, which is typically a non-nucleophilic base in solution, acts as a nucleophile under HSBM conditions. We were able to conduct the Tishchenko reaction, a transformation of an aldehyde to its dimeric ester, for a variety of aryl aldehydes. For example, benzyl benzoate, used in flavorings and fragrances, can be prepared under these conditions in >99% yield. The Tishchenko reaction is particularly environmentally friendly because it makes use of a catalyst and is 100% atom economic.

259. Novel Strategies for Complex Molecule Synthesis

Craig J. Forsyth, Department of Chemistry, The Ohio State University, Columbus, OH

Targeting the total synthesis of natural products has spawned many innovations in organic chemistry, ranging from new reaction discovery, methodology development, and novel strategies for the rapid enhancement of molecular complexity. Recent efforts in our labs towards the total synthesis of a range of structurally diverse natural products including azaspiracid-3, largazole, dinophysistoxins, phorboxazole A, and salvinorin A have provided advancement in all of these areas. Highlights of these will summarized.



260. A Fragmentation Route to Allenes

David G.J. Young, Chemistry, East Tennessee State University, Johnson City, TN and Mark-Henry Kamga, Chemistry, East Tennessee State University, Johnson city

The first fragmentation route to allenes is described. The route relies upon Diels-Alder cycloaddition of furan subunits with ketene equivalents followed by regiospecific enolate formation using reductive ring opening. Following oxygen differentiation, conversion to the vinyl triflate leads to ring cleavage and the formation of allene intramolecular nitrile oxide cycloaddition precursors. A table of fragmentation reactions will be presented.

261. Nano-Catalysts: Bridging the Gap Between Homogeneous and Heterogeneous Catalysis

Vivek Polshettiwar^1, Babita Baruwati^2 and Rajender S. Varma^2, (1)Sustainable Technology Division, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, Cincinnati, OH, (2)Sustainable Technology Division, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH

Functionalized nanoparticles have emerged as sustainable alternatives to conventional materials, as robust, high-surface-area heterogeneous catalyst supports. We envisioned a catalyst system, which can bridge the homogenous and heterogeneous system. Postsynthetic surface modification protocol for magnetic nanoparticles has been developed that imparts desirable chemical functionality and enables the generation of catalytic sites on the surfaces of ensuing metal-catalysts as well as organocatalysts. In view of their nano-size, the contact between reactants and catalyst increases dramatically thus mimicking the homogeneous catalysts. Their insoluble character coupled with paramagnetic nature, on the other hand, enables easy separation of these nanocatalysts from the reaction mixture using external magnet, which eliminates the requirement of catalyst filtration. These novel nano-catalysts blur the distinction between homogeneous and heterogeneous catalysis thus preserving the desirable attributes of both the systems. Their unique activity and high selectivity in several reaction types will be discussed.

262. Novel Green Catalytic Oxidation Reactions

Mo Hunsen, Ph.D., Zachary S. Grant and Phan T. Truong, Department of Chemistry, Kenyon College, Gambier, OH

Green chemistry has come to the forefront of science research in the last two decades. We have been active in pursuing green chemistry by way of catalytic reactions mainly green oxidation reactions and enzyme catalyzed organic reactions. Chromium reagents have been proven to be versatile oxidizing reagents and are important in organic transformations. Notable chromium reagents include the Jones reagent - chromic acid - and the mild Corey reagent - pyridinium chlorochromate. Due to its carcinogenicity, the chromium waste generated in these reactions is disadvantageous especially for large scale and industrial applications. We have developed new reactions for selective oxidation of carbohydrates and preparation of aldehydes, ketones, and carboxylic acids from alcohols. We use chromium reagents as catalysts and a secondary oxidant - that is recyclable or that does not generate toxic waste - to regenerate the chromium catalyst. As a secondary oxidant, we have used periodic acid that is recyclable by electrolysis. We also show that Oxone® - as a cheap secondary oxidant - is an excellent reagent to regenerate the chromium reagent. When Oxone is the secondary oxidant, the byproducts are simple potassium salts. Hence, using the chromium reagents as catalysts, we are able to reduce the amount of chromium waste generated by up to a 100 fold while maintaining the advantages of chromium oxidation reactions. It is even more interesting to note that the chromium waste can be reused as a catalyst by using fresh secondary oxidant. This presentations focuses on our recent results on green oxidation reactions.

Analytical Chemistry: Bioanalysis Focus

Organizer: Rebecca Whelan Oberlin College, Oberlin, OH
Presider: Rebecca Whelan Oberlin College, Oberlin, OH

Session Overview: This session highlights the application of analytical methods to systems of biological origin. Areas of emphasis may include analytical neurochemistry, bio/nanomaterials, sensors, proteomics/metabolomics, bioelectrochemistry, miniaturized bioanalysis platforms, separations, and mass spectrometry. Reports in instrument development and analytical application are both encouraged.

263. Quantitative Analysis of 6-Benzylthioinosine, A Promising Therapeutic Agent for Acute Myeloid Leukemia

Lan Li[1], David N. Wald[2], William Tse[3] and Yan Xu[1], (1)Department of Chemistry, Cleveland State University, Cleveland, OH, (2)Department of Pathology, Case Western Reserve University School of Medicine, Cleveland, OH, (3)Department of Pathology, Case Western Reserve School of Medicine, Cleveland, OH

Acute myeloid leukemia (AML) is characterized as the differentiation arrest and uncontrolled proliferation of myeloblasts. Thus, inducing differentiation of myeloblasts to maturation has become a promising therapeutic strategy for AML. This strategy was successfully applied to the treatment of acute promyelocytic leukemia (APL), a rare subtype of AML, with a differentiation inducing agent called all-trans retinoic acid (ATRA). While ATRA is only useful for APL subtype, a novel differentiation inducing agent, 6-benzylthioinosine (6BT), exhibits not only high myeloid differentiation-inducing activity but also specific cytotoxicity in a subset of leukemia cells. Therefore, 6BT is currently exploited as therapeutics for other AML subtypes. In this work, we developed and validated a liquid chromatography-tandem mass spectrometry (LC-ESI-MS/MS) method for the direct quantification of 6BT in both mouse and human plasma. A liquid-liquid extraction protocol was established by utilizing ethyl acetate as the extraction agent. Compound separation was carried out on an YMC-AQ® Column (2.0×50 mm) and the eluent was monitored by the positive-electrospray-ionization mass spectrometry (ESI^+-MS/MS). Quantification of the compound was realized by the multiple reaction monitoring (MRM) mode. Two linear calibration curves (3-1000 ng/mL) were established by utilizing 2-amino-6-benzylthioinosine (2A6BT) as the internal standard. After validation, the methods developed showed low matrix effect while high recovery, accuracy and precision. The method developed was also applied to an animal model and the preliminary pharmacokinetic study revealed that 6BT has a half-life of ca. 13 min in mice. The analytical method we developed will facilitate the therapeutic development of 6BT.

264. Molecular Targets for Diabetes Mellitus Associated Erectile Dysfunction

Elizabeth H. Yohannes, Ph.D.[1], Jinsook Chang, Ph.D.[2], Kelvin P. Davies, Ph.D.[2] and Mark R. Chance, Ph.D.[1], (1)Center for Proteomics and Bioinformatics, Case Western Reserve University School of Medicine, Cleveland, OH, (2)Department of Urology, Albert Einstein College of Medicine, Bronx, NY

Abstract

Protein expression profiles in rat corpora smooth muscle were compared between animal models of STZ-induced diabetes mellitus (STZ-DM) and age matched controls (AMC) at one week and two months. At each time point, protein samples from four STZ-DM and four AMC rat corpora tissues were prepared independently and analyzed together across multiple DIGE gels using pooled internal standard sample to quantify expression changes with statistical confidence. A total of 170 spots were differential expressed among the four experimental groups. A subsequent mass spectrometry analysis of the 170 spots identified a total of 57 unique proteins. The proteins that are specifically seen to be down regulated with diabetes include: isoforms of collagen that are precursors to fibrils forming collagen type 1; Hsp47, which assists and mediates the proper folding of procollagen; proteins whose abundance is controlled by sex hormones (e.g., CRP1, and A2U); On the other hand, proteins that are seen to be up regulated include: proteins involved in cell apoptosis (e.g., p53, 14-3-3-gamma, Serpinf1, Cct4, Cct5, and Sepina3n); proteins that neutralize the biological activity of nerve growth factor (e.g., Anti-NGF 30); and also proteins involved in lipid metabolism (e.g., ApoA1 and ApoA4). Further validation of p53, 14-3-3 gamma, and Hsp47 expression in the diabetic rat cavernosum using western blot demonstrated increased p53 and 14-3-3 gamma but decreased Hsp47. Taken together; our results broaden the ranges of candidate proteins mediated by diabetes that could account for the functional deficits and complications known to occur in erectile dysfunction.

265. Quantitative Determination Antineoplastic Agent Hexamethylene Bisacetamide in Mouse Plasma and Tissue by LC-MS/MS

Kerri Smith[1], Xiang Zhou[1], Monica M. Montano, Ph.D.[2] and Yan Xu[3], (1)Department of Chemistry, Cleveland State University, Cleveland, OH, (2)Department of Pharmacology, Case Western Reserve University, Cleveland, OH, (3)Chemistry, Cleveland State Universtity, Cleveland, OH

Hexamethylene Bisacetamide (HMBA), a polar basic compound, has recently been shown to have antineoplastic activity by inducing up-regulation of the antiproliferative breast cancer protein HEXIM1 (hexamethylene bisacetamide-inducible protein 1). Current tumorigenesis studies in mouse models demand a more sensitive method for the detection and quantification of HMBA than what is represented in the current liturature. Our lab is working to develop and validate according the FDA Guidelines an LC-MS/MS method for the quantitative determination of HMBA in human and mouse plasma and mouse mammary tissue using heptamethylene bisacetamide (7MBA) as the internal standard. This presentation will discuss the results of the work.

266. In Vitro Evaluation of Dopamine D2 and D3 Receptors in the Striatum Using Fast Scan Cyclic Voltammetry

Francis K. Maina and **Tiffany A. Mathews**, Department of Chemistry, Wayne State University, Detroit, MI

Doapamine (DA) has attracted much attention due to its involvement in: addiction, Schizophrenia, Parkinson’s disease and attention deficit hyperactivity disorder. The actions of DA are mediated by five receptor subtypes that can be grouped into two sub-families, D1-like and D2-like. The D2-like family is known to control DA release and is composed of D2, D3 and D4 receptors. The D3 receptor has a fairly restricted pattern of expression in the mammalian brain; specifically the localization of DA D3 receptors in the nucleus accumbens core and shell. The nucleus accumbens is of particular interest because this brain region is often associated with the rewarding properties of drugs of abuse. Using background subtracted fast scan cyclic voltammetry (FSCV), we are investigating the ability to measure activity of release-regulating DA D2 and D3 autoreceptors in the caudate-putamen and nucleus accumbens (core and shell). The carbon fiber microelectrode with a diameter of 7 microns allows for high spatial resolution to discriminate between core and shell of the nucleus accumbens. Preliminary studies using the D2 agonist quinpirole show no difference in DA release between the caudate-putamen and the nucleus accumbens. Using the D3 agonist (+)-PD128907 show a significant decrease in DA release in the core and shell of the accumbens compared to the caudate-putamen. The specificity of D2 or D3 receptor agonist was confirmed with the use of selective antagonists, which reversed the effects of the agonists. These preliminary results suggest that FSCV can be used to probe DA receptor functionality in the striatum.

267. Quantitative Determination of Cannabinoid Receptor Antagonist Surinabant by Chromatographic Methods

Melissa McCulloch, B.S. and Yan Xu, PhD, Department of Chemistry, Cleveland State Universtity, Cleveland, OH

Surinabant [5-(4-bromophenyl)-1-(2,4-dichlorophenyl)-4-ethyl-N-(1-piperidinyl)-1H-pyrazole-3-carboxamide] is a cannabinoid receptor type 1 antagonist which is believed to indirectly inhibit the dopamine-mediated reward system for food, alcohol and nicotine addiction. Currently, there is no analytical method reported for the determination of surinabant in biological matrices. In this work, a liquid chromatographic (LC) method with both ultraviolet (UV) and electrospray ionization tandem mass spectrometric (ESI-MS/MS) detection has been developed and validated for the quantitative measurement of surinabant in human plasma to support the clinical investigation of this new drug. The compound AM251 was used for internal calibration. A protein precipitation procedure was employed for plasma sample preparation. Chromatographic separation of surinabant and internal standard was carried out on a Waters YMC™ Pro C4 cartridge column using a mobile phase

containing 99.9% CH_3CN/H_2O (50:50, v/v) and 0.1% HCOOH. The LC-UV detection was accomplished by monitoring the absorption at 258 nm, which had an LLOQ of 100 ng/ml and a calibration range of 100-1500 ng/ml for surinabant. The LC-ESI-MS/MS detection was achieved using positive multiple-reaction-monitoring (MRM) mode for surinabant (m/z 523 → 423) and the internal standard (m/z 555 → 455), which had an LLOQ of 5.00 ng/ml and a calibration curve of 5.00-1000 ng/ml. The methods developed provide quantitative measures for surinabant in human plasma. The methods developed can be used for the pharmacokinetic study of surinabant in clinical trials, as well as, to study the modulation of CB receptors.

268. Sustained Intracellular Dosing of Molecules to Elucidate Cellular Function

Prasad Oruganti and Miklos Gratzl, PhD, Biomedical Engineering, Case Western Reserve University, Cleveland, OH

The introduction of specific molecules into single cells is a widely used approach to probe cellular mechanisms. Existing methods include the injection of discrete boluses of material using mechanical or electro-mechanical principles, and continuous perfusion from a patch pipette in the whole cell configuration. Here we report on a scheme to elucidate the dynamics of transport of fluorescent molecules within cells. We use a microscopic diffusion port called the Diffusional Microburet (DMB) inserted into the studied cell to effect slow and sustained dosing of molecules into the cytoplasm. Spreading and binding of the molecules in the entire cell are observed in real time with fluorescence microscopy. We also report on a method to estimate distribution of the molecules normalized to cell height within the cell as a function of time to provide information on local concentrations, independent of the shape and height of the cell.

We show the use of the combined DMB delivery and concentration measurement scheme in two applications: 1. Elucidating junctional permeability of connected A7r5 cells over long time periods (~30 min). We show the constancy of junctional permeability over these time scales and we report on cells exhibiting a decreasing junctional permeability indicative of dividing cells. 2. Distribution of the anticancer drug doxorubicin in NRKE cells during sustained intracellular dosing. We find that the distribution of doxorubicin is highly non-uniform and we also report on the finding that doxorubicin binds sequentially with distance from the dosing location to binding sites within the nucleus.

Art and Science

Organizer: Sharon Miller, Senior Research Engineer NASA Glenn Research Center, Cleveland, OH
Presider: Sharon Miller NASA-GRC, Cleveland, OH

Session Overview: Advances in science and technology have far reaching benefit to society. One of the areas benefiting from the use of science and technology is the conservation, preservation and authentication of works of art and symbols of our cultural heritage. In this session presenters share their expertise and experience using modern science and technology as a tool to aid in the conservation or authentication of art.

269. Science in the Service of Art: Materials Research at the Art Materials Information and Education Network

Mark D. Gottsegen, Materials Research Director and **Albert P. Albano, Executive Director**, Education Department, Intermuseum Conservation Association, Cleveland, OH

Abstract for CERMACS 2009
Science in the Service of Art: Materials Research at the Art Materials Information and Education Network

In this presentation the Executive Director of the Intermuseum Conservation Association (ICA) will discuss the work of the Art Materials Information and Education Network (AMIEN), part of the

Education Department at the ICA. After a brief historical introduction about the ICA and AMIEN, the scientific projects of the past 30 years, and current projects, will be described. All of these projects have been collaborations between scientists and artists and the outcomes have benefited both groups.
[75 words]

270. Energy Dispersive X-Ray Analysis of a Series of Early Nineteenth Century Korean Coins,

Danielle Garshott, Elizabeth MacDonald, Stephanie Spohn and Mark A. Benvenuto, Department of Chemistry & Biochemistry, University of Detroit Mercy, Detroit, MI

A series of early nineteenth century Korean coins composed of several subsets, based on character identifications, were analyzed using energy dispersive X-ray fluorescence (EDXRF) spectroscopy. The general casting of each sample was a round coin with a central, square hole, four characters on the obverse or head side, and up to two characters on the reverse or tails side. The entire sample set was examined by X-ray fluorescence multiple times. The composition of the coins varied, but routinely included copper, lead and zinc as major elements. Considerably smaller amounts of antimony, tin, iron, and silver were found in the sample set. The full findings are presented and discussed.

271. Corrosion Chemistry of Historic Lead-Tin Alloy Organ Pipes

Catherine M. Mauck and Catherine M. Oertel, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH

Atmospheric corrosion is a major cause of deterioration in lead-tin alloy organ pipes. Centuries-old organs stand as valuable documents not only of musical history but also of technological history, and an understanding of the causes and mechanisms of this corrosion is essential for their conservation. Organic acids, particularly acetic and formic acids, emitted from the wood of organ cases have been identified as significant corrosive agents. In order to study the role of alloy composition in the susceptibility of pipes to organic acid attack, lead-tin alloys containing 0-15% Sn were exposed to acetic acid vapor in laboratory exposure studies. Corrosion rates were monitored gravimetrically, and corrosion product phases were identified and analyzed using grazing incidence angle X-ray diffraction and scanning electron microscopy. The susceptibility of the alloys shows a strong dependence on relative humidity and a relatively weak dependence on the presence of surface sodium chloride.

Two of the compounds that have been identified as corrosion products on organ pipes, $Pb(CH_3COO)_2{\cdot}2PbO{\cdot}nH_2O$ and $Pb(CHOO)_2{\cdot}PbO$, had been previously characterized with powder X-ray diffraction fingerprints, but their structures had never been determined. Both compounds were crystallized using hydrothermal conditions, and structures were determined through single-crystal X-ray diffraction. These compounds may be viewed as extended inorganic-organic networks containing single and double chains of edge-sharing Pb_4O tetrahedra. In basic lead acetate, the acetate ligands further link the chains to form two-dimensional layers. In basic lead formate, the linkages provided by the formate ligands create a three-dimensional network.

272. Using the Space Environment to Conserve Art

Sharon Miller, Senior Research Engineer, Space Environment and Experiments Branch, NASA Glenn Research Center, Cleveland, OH and Bruce A. Banks, Consultant, Space Environment and Experiments Branch, Alphaport , Consultant to NASA Glenn Research Center, Cleveland, OH

Atomic oxygen, which is predominant in the low Earth orbit (LEO) environment, is very chemically reactive and combines with organic compounds on surfaces to create carbon monoxide, carbon dioxide and water vapor. Although it can cause issues for spacecraft flying in LEO, it does have some benefits here on Earth as a dry, non-contact method to clean surfaces of unwanted organic material.

In particular, it has been shown to be able to safely remove fire damage and lipstick imprints from the surface of art in situations where other chemical solvents were not able to be used. Examples will be shown of how atomic oxygen can be generated here on Earth, and how it has been used to conserve paintings.

273. Characterization of the Rock Art of Cueva La Conga, Nicaragua: Preliminary Results

Ruth Ann Armitage and Ran Li, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI

Cueva La Conga is the only known painted cave in Nicaragua, in a part of that country about which little is known archaeologically. The rock art, which includes carved rock formations as well as paintings and handprints, may provide clues about the past people and culture of this area. Archaeologists want to know if the paintings were influenced by the Maya to the north, or the Caribbean cultures to the east, or were a purely indigenous development. Determining the age of the paintings will help to understand the possible cultural relationships between known cultures and the rock art of Cueva La Conga. None of the rock art of Nicaragua has been dated before. Radiocarbon dating of the charcoal images is underway; however, dating the red, yellow, and purple images requires that an organic binder was used and remains to be extracted and dated using accelerator mass spectrometry to determine the ^{14}C content. We are using thermally assisted hydrolysis/methylation-gas chromatography-mass spectrometry (THM-GC-MS) to study the composition of the paints to determine if any binder material remains to be dated. We will compare the compositions of the paint and unpainted limestone to determine if a reliable date is likely to be obtained. This is the first comprehensive study where the chemical characterization of the paint was considered in the sampling of the rock art to be dated. We will describe the inherent difficulties of reconciling good analyses with preservation of these irreplaceable and at-risk cultural materials.

Computational Chemistry (3)

Organizer: Jane S. Murray Cleveland State University, Fairview Park, OH
Organizer: Peter Politzer Cleveland State University, Fairview Park, OH
Presider: Peter Politzer Cleveland State University, Fairview Park, OH
Presider: Jane S. Murray Cleveland State University, Fairview Park, OH

Session Overview: Acknowledgements: We greatly appreciate the support provided by the U. S. Office of Naval Research and the Computers in Chemistry Division of the American Chemical Society.

274. Carbon Nanotubes for Sensor Design and Nonlinear Optical Applications: Density Functional Theory Studies

Felipe Bulat, Global Strategies Group (North America) Inc, Crofton, MD

Carbon nanoubes have found application in very diverse fields, from medicine to structural composites and nano electronics. I will discuss how some of their remarkable properties lead to applications as key components in sensor design and non-linear optical materials. In particular I will focus on the opportunity that crossed-nanotubes junctions offer as electromechanical devices, and the manner in which our detailed computational studies have provided key insight into how their performance can be maximized. I will also discuss the novel donor-nanotube paradigm for the effective design of materials with large first hyperpolarizabilities, as suggested by our investigations into their response properties. The Average Local Ionization Energy and Electrostatic Potential maps on their molecular surfaces furnish an excellent handle on this and other materials properties and I will highlight some relevant research along these lines.

275. Computational Study of the Stone-Wales Defect in Armchair Single-Walled Carbon Nanotubes

T. C. Dinadayalane, Ph.D and Jerzy Leszczynski, Department of Chemistry, Jackson State University, Jackson, MS

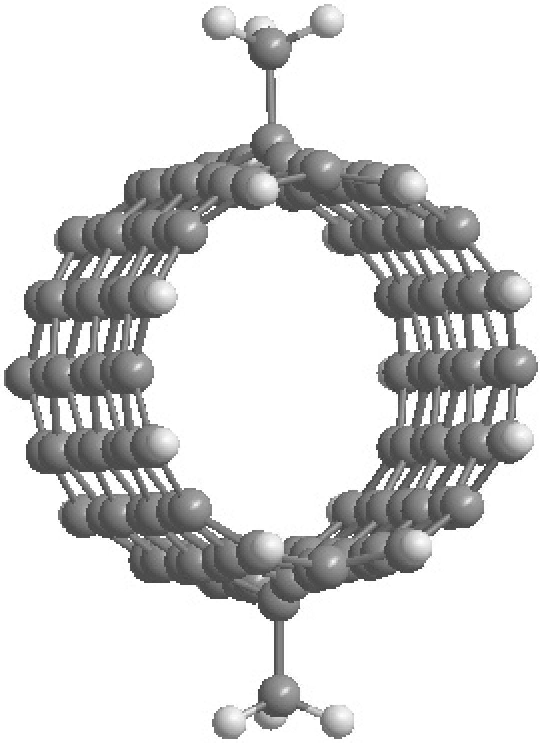
Carbon nanotubes (CNTs) possess outstanding structural, electronic and mechanical properties. Hence, they are considered to make materials for defense and several other day-to-day life applications in diversified areas. Carbon nanotubes are not always formed as perfect structures as we think. Experimental and theoretical studies demonstrated that defects such as vacancies, Stone-Wales (SW) defects, pentagons, heptagons, dopants may exist in the nanotubes. Stone-Wales defect, which can be created by a 90° rotation of a C-C bond in a hexagonal network of the carbon nanotube, is one of the most important defects in the single-walled carbon nanotubes (SWNTs). Using density functional theory calculations, we have investigated the Stone-Wales defect formation with two different orientations in a range of armchair SWNTs. The variation of defect formation energies by changing the diameter of the tube is examined. We have investigated the changes of band gap between the perfect and Stone-Wales defect SWNTs considered and how the Stone-Wales defect formation energy varies by changing the defect position in (5,5) SWNT. We have measured and analyzed the pyramidalization angles at carbon sites in the Stone-Wales defect region. Our study indicates that the C-C bond shared by two heptagons in the SW defect of SWNTs need not always be less reactive than the corresponding bond in the pristine structure and the reactivity of that bond depends on the orientation of the defect in the SWNT.

Acknowledgements: HPCDNM Project funded by the Department of Defense (DoD) through the U.S. Army/ERDC (Vicksburg, MS); Contract #W912HZ-06-C-0057. ONR grant (08PRO2615-00/N00014-08-1-0324).

276. Computational Investigation of Hydrogen and Methyl Chemisorption to Carbon Nanotube Models

Ronald C. Brown, Ph.D., Department of Chemistry & Biochemistry, Mercyhurst College, Erie, PA

Models for carbon nanotubes were designed and used to determine the relative energetics of hydrogen and methyl chemisorption as a function of nanotube size, nanotube geometry, and the local adsorption environment. Computational models designed to simulate zigzag `(n,0)` [n = 5 to n = 9], and armchair `(n,n)` [n = 3 to n = 6] nanotube geometries were truncated to produce cross-sections of single-walled carbon nanotubes (SWNT). The dangling bonds at the ends of the cross-sections were capped with hydrogen atoms. The radii of the cross-sectional models ranged from 2.2 Å to 4.4 Å. Initially, models with clean surfaces were fully optimized using density functional theory. Calculations were then performed on rigid tube models with hydrogen or methyl adsorbates. Finally, the geometries of the models with adsorbates were allowed to fully relax. All calculations were performed at the B3LYP/6-31G** level. The process allowed both the binding energies to rigid tubes and the tube relaxation energies to be determined. The results of this study include a comparison of the adsorption energetics and fully relaxed nanotube-adsorbate geometries (i) between zigzag and armchair tubes; (ii) as a function of tube radius; and (iii) as a function of the quantity and location of adsorbates.



277. *E-Z* Photoisomerization of Diphosphenes: The Involvement of a Dark Phantom State

John L. Payton, Graduate Student , Department of Chemistry, Case Western Reserve University, Cleveland, OH and M. Cather Simpson, Professor of Chemistry, Departments of Chemistry and Physics, The University of Auckland, Auckland, New Zealand

Over the past several decades there has been a heightened interest in molecular devices such as molecular switches, organic light emitting diodes (OLED's), molecular wires, and numerous other molecularly engineered devices. These devices are generally organic based materials that tend to exploit E-Z isomerization of carbon-carbon, nitrogen-nitrogen, and/or carbon-nitrogen double bonds. As robust and intriguing as the current literature is on these compounds, many have neglected the possibility of substituting heavier main group elements, such as phosphorus, into such systems. Newer heavier atom based systems may introduce different properties that currently are not available to their lighter atom based cousins. Here we have used high-level computational methods to study the E-Z isomerization of aryl-diphosphenes (i.e., Ar-P=P-Ar), exploring both the thermal process and excited energies and geometries during the three proposed pathways. Those pathways are rotation about the central phosphorus-phosphorus double bond (i.e., C-P=P-C), in-the-plane inversion about the P=P-C bond angle, and dissociation of the phosphorus-phosphorus double bond. CASPT2 calculations will be presented on the three proposed pathways showing that conical intersections play a key role in photoisomerization of diphosphenes and the population of a dark state.

Energy Storage and Energy Conversion: Fuel Cells

Organizer: Aloysius Hepp, Ph.D. NASA Glenn Research Center, Cleveland, OH
Organizer: Prashant Kumta, Ph.D. University of Pittsburgh, Pittsburgh, PA
Presider: M.J. Kulis, Ph.D. The NCSER, Cleveland, PA

Session Overview: This session consists of two invited and two contributed talks. The focus of the session is primarily on carbon-based materials. The applications of these materials are diverse including hydrogen storage, de-sulfurization, and catalyst supports. The materials systems described in this session have potential for use in a variety of fuel cell technologies.

278. Chemical Durability Study of Non-Perflorinated Materials for Fuel Cell Membranes

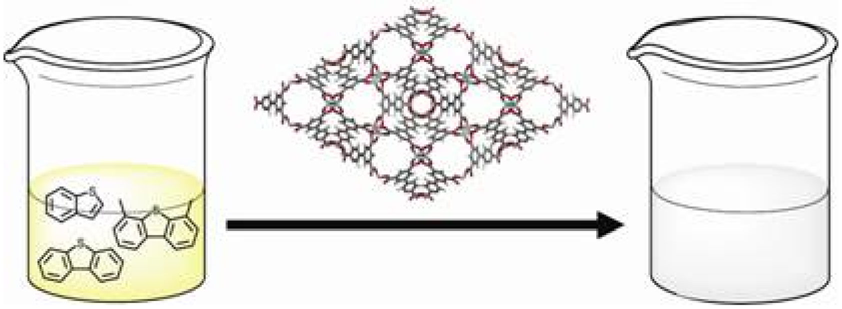
Deepa Savant[1], David A. Schiraldi[1] and Thomas A. Zawodzinski[2], (1)Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, (2)Department of Chemical Engineering & Case Applied Power Institute, Case Western Reserve University, Cleveland, OH

Model compounds representing portions of a range of aromatic (non-perfluorinated) polymers under consideration for use as polymer electrolyte fuel cell membranes were studied under simulated fuel cell degradation conditions. The selected model compounds were exposed to both Fenton's degradation and UV/peroxide test conditions and the degradation products were then confirmed using liquid chromatography-mass spectrometry as the major analytical tool. The major degradation products observed range from mono- and di-hydroxylated model compounds to extensive hydroxylation and dimerization. Some of the model compounds with more than one sulfonic acid groups may show desulfonation under these test conditions which may or may not be due to the hydroxyl radicals.

279. Liquid Phase Adsorption by Microporous Coordination Polymers for the Desulfurization of Fuels

Katie A. Cychosz, Antek G. Wong-Foy and Adam J. Matzger, Department of Chemistry, University of Michigan, Ann Arbor, MI

The desulfurization of transportation fuels is the subject of renewed interest because sulfur levels less than 0.1 parts per million are necessary to develop fuel cells reliant on onboard reforming of hydrocarbons to hydrogen. Large organosulfur species found in diesel, for example, are difficult to remove using current industrial processes. Adsorption to porous solids is an attractive method for removal of these compounds that has recently garnered attention. Better sorbents are required for practical applications and microporous coordination polymers (MCPs) are high surface area, high porosity materials with demonstrated capability to adsorb small molecules. An assortment of MCPs with various surface areas and pore sizes have been tested in equilibrium and packed bed experiments in order to determine the adsorption capacity of these MCPs for organosulfur compounds. It was determined that adsorption capacity does not correlate with surface area or pore volume, as might be expected based on published gas adsorption results, but rather on a pore size and shape where interaction between the organosulfur compound and the MCP is maximized. Additionally, MCPs were found to exhibit extremely high capacity for 4,6-dimethyldibenzothiophene, the organosulfur compound that is most difficult to remove using current catalytic techniques. The competition between the organosulfur compounds and other aromatic compounds found in fuels has been studied, as well as the thermal regeneration of the MCPs. This work represents one of the first examples of liquid phase adsorption using these materials and the high capacities obtained indicate that this will be an important application for MCPs.



280. Novel Carbon Supports for Electrocatalysts in PEM Fuel Cells

Abhishek Guha, Contained Energy LLC, Cleveland, OH, David A. Schiraldi, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH and Thomas A. Zawodzinski, Department of Chemical Engineering & Case Applied Power Institute, Case Western Reserve University, Cleveland, OH

Novel carbon structures such as carbon nanofibers and activated carbon possess enormous potential as support materials for electrocatalysts such as platinum employed in PEM fuel cell electrodes. Usefulness of such carbons is contingent upon the catalyst particles being deposited very finely and homogeneously onto the carbon support surface. Chemical functionalization of the carbon surface has been shown to be a critical requirement for optimum platinum deposition. Additionally, a variety of others factors play a key role, such as the extent of surface functionalization and experimental parameters involved in the platinum deposition process. In this work, the ‘colloidal' method of supported catalyst synthesis has been employed for homogenous deposition of platinum catalyst on the novel functionalized carbon supports, under optimized preparation conditions. A relationship has been established between variation in platinum particle size with nature of the chemically modified carbon surface, its surface treatment and processing variables. Electrochemical characteristics of the supported catalyst such as the electrochemically active surface areas have been determined by cyclic voltammetry; while rotating disk electrode studies have been carried out to classify catalytic activity towards oxygen reduction reaction (ORR). Membrane Electrode Assemblies (MEA) have been fabricated using the supported catalysts and Nafion® membranes. Fuel cell performances for the MEAs have been reported as current-potential polarization curves. An attempt has been made to isolate and identify the influence of electronic conductivity of the support and its microstructure within an MEA, on the corresponding polarization behavior.

281. Hydrogen Storage in Microporous Coordination Polymers: A Technology Update

Antek G. Wong-Foy, Kyoungmoo Koh and Adam J. Matzger, Department of Chemistry, University of Michigan, Ann Arbor, MI

Microporous coordination polymers (MCPs) have attracted significant attention as potential adsorbents for various gas storage applications; foremost among these is in the area of hydrogen gas storage. In particular, gravimetric hydrogen storage capacity is a property that has been correlated with surface area for MCPs and significant improvement will be needed to achieve US Department of Energy system targets of 6.0 wt% (45 g/L) by 2010. Although over a thousand MCPs have been reported, only a few possess surface areas higher than that of the highest surface area activated carbon, AX-21. Here, we present our approaches for achieving ultra-high surface area MCPs and their saturation H_2 uptake at 77 K where the type of pore contributing to the surface area has a profound effect on H_2 capacity.

Functional Materials: Biofunctional Materials (3)

Organizer: Joerg Lahann University of Michigan, Ann Arbor, MI
Organizer: Horst A. von Recum Case Western Reserve University, Cleveland, OH
Presider: Horst A. von Recum Case Western Reserve University, Cleveland, OH
Presider: Joerg Lahann University of Michigan, Ann Arbor, MI

282. Molecular Programming with DNA

Erik Winfree, Computer Science, Computation & Neural Systems, Bioengineering, California Institute of Technology, Pasadena, CA

Information can be stored in molecules and processed by molecular reactions. Molecular information processing is at the heart of all biological systems; might it soon also be at the heart of non-biological synthetic chemical systems? Perhaps yes. One technological approach comes from DNA nanotechnology and DNA computing, where DNA is used as a non-biological informational polymer that can be rationally designed to create a rich class of molecular systems -- for example, DNA molecules that self-assemble precisely, that fold into complex nanoscale objects, that act as mechanical actuators and molecular motors, and that make decisions based on digital and analog logic. I will argue that to fully exploit their design potential, we will need to invent programming languages for specifying the behavior of information-based molecular systems, to create theoretical tools for understanding and analyzing the behavior of molecular programs, to develop compilers that automate the design of molecules with the desired behaviors, and to expand experimental techniques so that the implementation and debugging of complex molecular systems becomes as commonplace and practical as computer programming.

283. Designed Peptide Conjugates for Directing the Simultaneous Synthesis and Assembly of Complex Nanoparticle Superstructures

Nathaniel L. Rosi, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA and Chunlong Chen, Chemistry, University of Pittsburgh, Pittsburgh, PA

We describe a new general methodology for rationally organizing nanoparticles into complex nanoparticle superstructures. This methodology relies on the careful design of peptide conjugate molecules that direct both the synthesis and assembly of nanoparticle superstructures. Importantly, the synthetic methods described allow for 1) the design and preparation of topologically complex structures, 2) precise control over the placement of nanoparticles within the structure, 3) control of nanoparticle compostion, and 4) control over the registry of nanoparticles with respect to one another within the superstructure. We illustrate the utility of this methodology by showing how it can be used to prepare various nanoparticle superstructures, including 1-D particle chains, gold nanoparticle double helices, and quadruple helices and we also show how the structural parameters of these superstructures can be tailored.

284. Preparation and Characterization of Superlowfouling Electrospun Scaffolds of Zwitterionic Polysulfobetaine Methacrylate for Tissue Engineering Applications

Reza Lalani, Lingyun Liu and Bo Zhang, Chemical and Biomolecular Engineering, University of Akron, Akron, OH

Zwitterionic surfaces and hydrogels have been previously studied for their superlow biofouling characteristics, a quality essential to biomaterials and tissue engineering. However in order to be useful as tissue-engineered constructs, scaffolds are needed. Electrospinning has been shown to produce continuous, porous, and fibrous matrix mimicking the structures of native extracellular matrix. Here we have prepared fibrous scaffolds of polysulfobetaine methacrylate (pSBMA) for their potential biomedical applications by electrospinning. Zwitterionic monomer, [2-(methacryloxy)ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide, was polymerized in ethanol solution using sodium bisulfite and ammonium persulfate as initiators to afford pSBMA. In order to bring pSBMA into solution for electrospinning, a minimum amount of salt was added to the aqueous solution of pSBMA, which was subsequently electrospun to produce nanofibrous scaffold. The effect of solution viscosity on the fiber diameter was studied. In addition, the effect of initiator concentrations on the polymerization of SBMA and the fabricated scaffolds was investigated. Further studies are under way to fabricate crosslinked electrospun scaffolds and test for their biological properties and biocompatibility.

285. Cyclodextrin Based Hydrogel Coatings for Antibiotic Drug Delivery

Thimmareddy Thatiparti and Horst A. von Recum, Department of Biomedical Engineering, Case Western Reserve Univesity, Cleveland, OH

Surgical site infections are usually treated with high dosage oral antibiotics. This administration route is suboptimal due to systemic side-effects and patient compliance. Therefore, it is imperative to develop new ways to deliver antibiotics locally to improve patient compliance by decreasing dosing frequency as well as to avoid the selection and spread of resistant bacteria. Since antibiotic overuse and misuse have led to the positive selection of bacteria which are resistant to most antibiotics. Therefore, we have developed a β-cyclodextrin (β-CD) based hydrogel coatings for surgical devices and for easy loading of antibiotics into a device to treat surgical site infections. Loaded antibiotics were expected to form an inclusion complex with β-CD in the hydrogel to subsequently controls drug release by affinity mechanisms for slower release than pure diffusion. In this work we explored novel β-CD based hydrogels by varying type and concentration of crosslinkers and optimized the gel synthesis conditions. For comparison, dextrose based gels were prepared with same crosslinkers. The optimized gels were characterized by NMR, DSC, WXRD, FTIR and ESCA. Eventually, the gels were loaded with three different antibiotics by common solvent method. The loading efficiency was estimated and release kinetics were conducted `in vitro`. As expected, the release of the drug, from β-CD based gels, was slower than that of dextrose gels (diffusion only controls) which indicated that the antibiotics form inclusion complex with β-CD. These hydrogels, therefore, could be useful to coat devices and release antibiotics for the treatment of surgical site infections.

286. Effect of the Attachment of An Oligomerization Domain On the Thermal Behavior of Elastin-Like Polypetpides

James T. Cole, Ali Ghoorchian and Nolan B. Holland, Department of Chemical & Biomedical Engineering, Cleveland State University, Cleveland, OH

Elastin like polypeptides (ELPs) are an emerging class of biomaterials due to their unique group of chemical, physical, and biological properties. We have constructed a library of ELPs based on the pentapeptide amino acid repeat sequence Gly-Val-Gly-Val-Pro (GVGVP). These polypeptides exhibit lower critical solution temperature (LCST) transition behavior from a soluble phase below the transition temperature to an insoluble two phase system above the transition temperature. This process is completely reversible so that they become soluble again upon lowering the temperature. This temperature can be tuned in many different ways at the molecular level by changing the molecular weight of the ELP. Solution parameters such as sample concentration and NaCl concentration can also change the transition temperature of the ELP. An oligomerization domain was incorporated at the end of the ELPs to form a poly(GVGVP) trimer, which was confirmed using SDS-PAGE. The transition temperatures of poly(GVGVP) and the poly(GVGVP) trimer solutions were measured using ultraviolet spectrophotometry over a range of sample concentrations, chain lengths, and solution properties. The oligomerization domain is found to reduce the transition temperature of the ELPs in comparison to linear ELPs of equal mass concentration for a wide range of concentrations.

Organic Chemistry (1)

Sponsor: Quanta BioDesign, Ltd., Toledo Section of the ACS
Organizer: Steven J. Sucheck University of Toledo, Toledo, OH
Presider: Steven J. Sucheck University of Toledo, Toledo, OH

Session Overview: The General Organic Symposium is open to all papers concerning subject matter relevant to the field of organic chemistry.

287. Synthesis of Anthracene Derivatives as Donor-Acceptor Liquid Crystal Components

Joseph J. Reczek, Mitchell Legg and Alex Murray, Department of Chemistry and Biochemistry, Denison University, Granville, OH

Columnar liquid crystals, composed of pi-stacked aromatic molecules, have excellent potential as components in organic electronic materials due to their ability to self-assemble and transport charge. Mixing combinations of some electron-rich and electron-poor aromatic molecules can alter and enhance these properties from those of the individual components. However, the affects of mixing are difficult to predict. Described here is the design, modeling, and synthesis of several complementary anthracene derivatives for investigation of the structure-property relationships in these mixed columnar liquid crystals. Characterization of their individual and combined properties is discussed.

288. Decarboxylative Condensation Between O18-Labeled Phenylpyruvic Acid and N-Hydroxyphenethylamine Affords O16-Amide Products

Rommel S. Talan, Aditya K. Sanki and Steven J. Sucheck, Department of Chemistry, University of Toledo, Toledo, OH

The decarboxylative condensation between α-ketoacids and hydroxylamines occurs by one of two competing mechanism to provide the amide product. The reaction can proceed through an imidic acid, Pathway A, or nitrilium ion intermediate, Pathway B. The isolation of oxazole byproducts from this reaction indicated that the hydroxylamine could cyclize on the nitrilium ion intermediate, followed by aromatization. A decarboxylative condensation between O^{18}-labeled phenylpyruvic acid and N-hydroxyphenethylamine resulted in amide products with complete loss of the label, indicating that Pathway B is the operative mechanism. The successful preparation of an O^{18}-labeled amide by alternative synthesis shows that the label is lost during the amidation reaction.

289. Synthesis of Transition State Inhibitors of Antigen 85

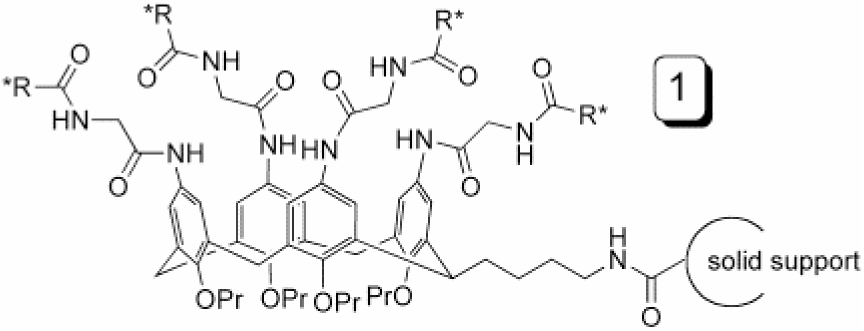
Aditya K. Sanki, **Fransis E. Umesiri**, Julie Boucau, Donald R. Ronning and Steven J. Sucheck, Chemistry, The University of Toledo, Toledo, OH

Enzymes involved in the synthesis and maintenance of the bacterial cell wall are frequently the targets of new anti-infective agents. In this work, a series of trehalose- and arabinose-based compounds were designed, synthesized and evaluated for their ability to inhibit antigen 85 (ag85), a complex of acyltransferases found in mycobacteria. Arabinose and trehalose were selected as starting points for inhibitor design since both are substrates for ag85. Arabinose methyl glycoside as well as trehalose were modified at the hydroxymethyl moiety with either a methyl ester, an a-keto ester, or an a-keto amide. The former being a potential suicide substrate capable of forming a covalent bond with serine at the Ser-His-Glu catalytic triad of ag85, with the latter acting as a potential transition state inhibitors.

290. Calixarenes for Attachment to Surfaces Via the Methylene-Bridge Position

Jordan L. Fantini, Michael J. Hardman and Ashley M. Thomas, Department of Chemistry & Biochemistry, Denison University, Granville, OH

The deprotonation of tetramethoxy-`p`-`tert`-butylcalix[4]arene at a single methylene-bridge position with butyl lithium yields an intermediate that reacts with a wide variety of electrophiles. Reaction with 1-bromo-4-chlorobutane results in the installation of a 4-chlorobutyl group at one methylene-bridge position on the calixarene. Through further modifications of this linker and of the upper- and lower-rim positions of the calixarene, substantially modified calixarenes may be attached to solid supports (depicted as **1**). The utility of these compounds may encompass the detection and separation of neutral and ionic species. Chiral groups on the calixarene allow for the possibility of resolution of enantiomers. This presentation will describe our recent results in the synthesis and characterization of the calixarenes suitable for attachment to a solid support.



291. Ultrafast UV-Vis and Infrared Spectroscopic Studies On Singlet Styrylcarbomethoxy Carbene

Yunlong Zhang, Jacek Kubicki and Matthew S. Platz, Department of chemistry, The Ohio State University, Columbus, OH

Diazo esters and ketones have been studied with ultrafast time-resolved spectroscopies, and the direct detection of produced singlet carbenes indicates that singlet carbenes are greatly stabilized by the neighboring carbonyl groups and have interesting inter- and intramolecular reactions. In this study, singlet carbenes with a neighboring C=C double bond was subjected to ultrafast time-resolved studies. Ultrafast infrared spectroscopy (270 nm excitation) with methyl styryldiazoacetate in chloroform detected two transient absorptions at 1705 cm^{-1} and 1765 cm^{-1}. Both bands were assigned to the cyclopropene produced from singlet styrylcarbomethoxy carbene via intramolecular cyclopropanation. This assignment is in excellent agreement with prediction of B3LYP/6-31+G(d) calculations. The singlet styrylcarbomethoxy carbene lifetime (32 ps), as determined by the intensity integration of the cyclopropene product, is much shorter than other singlet carbonyl carbenes, in consistent with the rapid intramolecular reaction. In the 1630-1660 cm^{-1} region, a broad transient was observed. The decay of this broad transient band is correlated with the growth of cyclopropene product, and hence it is assigned to singlet styrylcarbomethoxy carbene. In consistent with this assignment, ultrafast UV-Vis spectroscopic studies (310 nm) observed transient absorptions at 390 nm and 450 nm. The 390 nm band is assigned to the singlet carbene, in consistent with B3LYP calculations. The 450 nm band is temporarily assigned to triplet carbene.

292. Design and Synthesis of New Epothilone Analogues

Liyanaaratchige Tillekeratne and Mamoun M. Alhamadsheh, Department of Medicinal and Biological Chemistry, College of Pharmacy, University of Toledo, Toledo, OH

Epothilones were isolated from the cellulose-degrading soil bacterium `Sorangium cellulosum` in the search for anticancer agents with paclitaxel-like mechanism of action. They bind to the paclitaxel binding site on tubulin heterodimer and, like paclitaxel, they stabilize microtubules and inhibit cell division by disrupting microtubule dynamics. A number of salient properties in comparison to paclitaxel such as their simpler structure, higher water solubility and efficacy against multiple drug resistant cell lines produced a surge in epothilone research. Many analogues have been synthesized and much information has been generated on their SAR. We have synthesized two new classes of conformationally-constrained and open-chain epothilone analogues in which the key functionalities known to be required for biological activity have been retained. The design, synthesis and cytotoxic properties of some of these analogues will be presented.

Physical Chemistry (1)

Sponsor: American Chemical Society - Physical Chemistry Division, Newport/ Spectra-Physics, Ultrafast Systems, Coherent, Optronix
Organizer: Sarah J. Schmidtke College of Wooster, Wooster, OH
Organizer: Carlos E. Crespo-Hernández Case Western Reserve University, Cleveland, OH
Presider: Sarah J. Schmidtke College of Wooster, Wooster, OH
Presider: Carlos E. Crespo-Hernández Case Western Reserve University, Cleveland, OH

Session Overview: Talks in the general Physical Chemistry sessions include a focus on Photo-Organic Chemistry, Biophysics, and Ultrafast Excited-State Dynamics. There will also be presentations on current studies, outside of these areas, that fall within the larger field of Physical Chemistry.

293. Ultrafast Dynamics of Flavins and Flavoproteins

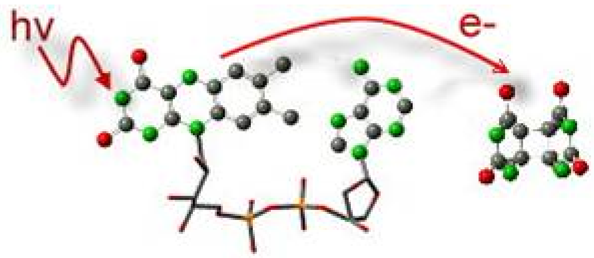
Dongping Zhong, Departments of Physics and Chemistry, The Ohio State University, Columbus, OH

Flavin molecules are one of the most important cofactors and chromophores in biology and flavoproteins have a variety of biological functions such as involving redox reaction, DNA repair, photoreceptor and even apoptosis. We report here systematic studies of photophysics and photochemistry of flavins in solution and in several proteins. Various ultrafast processes are observed and such studies are important to understanding molecular mechanisms of various biological functions by flavoproteins.

294. The Role of Adenine in the Excited State Behavior of Flavin Cofactors

Ksenija D. Glusac, Department of Chemistry, Bowling Green State University, Bowling Green, OH

We present a study of excited state behavior of reduced flavin cofactors using femtosecond optical transient absorption spectroscopy. The reduced flavin cofactors studied were in two protonation states: flavin-adenine dinucleotide ($FADH_2$ and $FADH^-$) and flavin-mononucleotide ($FMNH_2$ and $FMNH^-$). We find that $FMNH^-$ exhibits multi-exponential decay dynamics due to the presence of two bent conformers of the isoalloxazine ring. $FMNH_2$ exhibits an additional fast deactivation component that is assigned to an iminol tautomer. Reduced flavin cofactors also exhibit a long-lived component that is assigned to semiquinone and hydrated electron produced upon photoinduced electron transfer to solvent. The presence of adenine in $FADH_2$ and $FADH^-$ further changes the excited state dynamics due to intramolecular electron transfer from isoalloxazine to adenine moiety of cofactors. This electron transfer is more pronounced in $FADH_2$ due to p-stacking interactions between two moieties.



We further studied cyclobutane thymine dimer (TT-dimer) repair via FADH$^-$ and FMNH$^-$, and found that the repair is much more efficient in the case of FADH$^-$ cofactor. These results suggest that the adenine moiety plays a significant role in the TT-dimer repair dynamics. Two possible explanations for the adenine mediation are presented: (i) a two-step electron transfer process, with the initial electron transfer occurring from flavin to adenine moiety of FADH$^-$, followed by a second electron transfer from adenine to TT-dimer; (ii) the increased pre-concentration of TT-dimer molecules around the flavin cofactor due to the hydrophobic nature of adenine moiety.

295. Cis - Trans Isomerization as a Mean to Release Alcohols

Anna Gudmundsdottir, Sridhar Rajams and Tara Inman, Department of Chemistry, University of Cincinnati, Cincinnati, OH

We have designed novel photoremovable protecting groups (PPGs) that release alcohol efficiently upon exposure to light. The photorelease from these PPGs is initiated by cis-trans isomerization. The reaction mechanism was elucidated using transient spectroscopy, calculations and product studies. We will compare the rate of release from these PPGs to PPGs that rely on photoenolization to release alcohols

296. Photoinduced Rearrangement and Energy Flow in Small Polyatomic Molecules in Solution

Igor L. Zheldakov[1], Patrick Z. El-Khoury[1], Maxim S. Panov[1] and **Alexander N. Tarnovsky**[2], (1)Chemistry, Bowling Green State University, Bowling Green, OH, (2)Department of Chemistry and The Center for Photochemical Science, Bowling Green State University, Bowling Green, OH

One of the main challenges in the field of reaction dynamics is an understanding of how ultrafast processes are affected by the environment. Femtosecond pump-probe results concerning ultrafast excited-state relaxation and photoaquation will be presented for a model aqueous $PtBr_6^{2-}$ complex. A second topic is the photophysics/photochemistry in highly excited electronic states of solvated CH_2I_2. If time allows, the formation of molecular iodine from electronically excited CF_2I_2 will also be discussed.

297. Microwave Spectra of π-, μ-, and σ-Cyanophenol and Internal Rotation of π-Cyanophenol

Andrew R. Conrad, Nathan Z. Barefoot and Michael J. Tubergen, Department of Chemistry, Kent State University, Kent, OH

Fourier-transform microwave (FTMW) spectroscopy is one of the highest resolution spectroscopic techniques, and FTMW spectra are easily able to distinguish rotational transitions arising from different conformations of the same species. Fourier-transform microwave spectroscopy also serves as a powerful tool for investigating structure, hydrogen-bonding, conformational preferences, and internal rotation effects. Rotational spectra of the o-, m- and p-cyanophenol monomers have been measured in the range of 10.5 - 21 GHz using a Fourier-transform microwave spectrometer. The rotational transitions were fit using Watson's A-reduction Hamiltonian coupled with nuclear quadrupole coupling interaction terms for the ^{14}N nuclei. Ab initio calculations at the MP2/6-311++G** level predict the cis conformer of o- and m-cyanophenol to be more stable due to the intramolecular hydrogen bonding interaction between the hydroxyl hydrogen and the cyano nitrogen. The cis and trans conformers have been observed for m-cyanophenol; only the cis conformer has been observed for o-cyanophenol. Rotational transitions of the p-cyanophenol monomer are split due to the symmetric internal rotation of the hydroxyl group with respect to the aromatic ring; the barrier to internal rotation of the hydroxyl group has been determined from the splitting.

SAS/AVS Applied Spectroscopy Symposium (1)

Sponsor: De Nora Tech ThermoFisher Scientific Bruker BioSpin Corporation Shimadzu Scientific Instruments, Inc.
Organizer: Brian Perry LORD Corporation, Erie, PA
Organizer: Wayne Jennings, Ph.D. Case Western Reserve University, Cleveland, OH
Presider: Wayne Jennings, Ph.D. Case Western Reserve University, Cleveland, OH

Session Overview: The SAS/AVS symposium will feature papers on the utilization of spectroscopy for academic and industrial applications. The SAS/ACS Yeager Award talk for outstanding undergraduate research involving spectroscopy will also be featured in the symposium.

298. A Novel Narrow Band Electronically Tunable Image Filter

Nick Pallas, Department of Chemistry, Cleveland State University, Cleveland, OH and John F. Turner II, Department of Chemistry, Cleveland State University, Brooklyn, OH

Chemical imaging is an adaptation of hyperspectral imaging in which the hyperspectral data is used to create a single image that has chemically relevant contrast. Today's widefield hyperspectral imagers employ a variety of wavelength selection devices that include fixed band pass filters, acousto-optic tunable filters (AOTF), liquid crystal tunable filters (LCTF), etalons, and angle tuned filters. While fixed filters have the advantage of narrow pass bands and higher throughputs, their fixed transmittance wavelengths limit the practical number of bands that can be sampled. Likewise, the free spectral range of etalon filters is limited in practice to within one octave bandwidth across the central airy disk portion of the filter. Consequently, the AOTF and LCTF devices presently provide the largest free spectral ranges and have the added advantage of imparting little or no image distortion. In our work, we are developing the next generation of electronically tunable filters with narrower transmittances and higher throughputs than either the LCTF or AOTF. The technology under consideration makes use of a virtually imaged phased array (VIPA) that is coupled to a surface plasmon tunable filter (SPTF). In its current configuration, the device is suitable for narrow-band (<0.25nm FWHM) line scan imaging applications across comparably large free spectral ranges. We present a theoretical discussion of the SPTF-VIPA hybrid and compare its performance with the acousto-optic tunable filter, Fabry-Perot filter, and liquid crystal tunable filter.

299. XPS and TOF-SIMS Depth Profiling of Organic Materials Using C60 Sputtering

Scott R. Bryan, Gregory L. Fisher, John F. Moulder, Sankar Raman and Saad Alnalbulsi, Physical Electronics, Chanhassen, MN

Depth profiling of materials by XPS or TOF-SIMS is well established for inorganic materials. However, in the case of organic materials, depth profiing has been limited to elemental analysis due to damage of the organic structure during the sputtering process. The development of C60 ion beams has made it possible to depth profile many organic molecules by XPS and TOF SIMS for the first time. Because it has a different sputtering mechanism, C60 does not accumulate damage in the organic matrix like is observed for an atomic ion beam such as argon. Many new technologies in alternative energy and biomaterials, such as organic LED's and drug eluting stents, depend on higly engineerd organic thin films for their function. The use of C60 as a sputter beam has made it possible to acquire molecular depth profiles of many of these technolgically important materials. In this presentation, advances in organic depth profiling by XPS and TOF-SIMS will be presented.

300. In-Situ Ion-Beam Studies of Electrochemical Systems

Jesse S. Wainright, Ph.D., Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH

The spectroscopic techniques suitable for probing electrochemical systems in-situ are typically based on photon probes (e.g., infrared, or X-ray spectroscopies). However, spectroscopic techniques based on ion-beam probes, such as Rutherford backscattering Spectroscopy (RBS) and nuclear reaction analysis, can also be employed. In these applications, proton or alpha particle probes are extracted from the vacuum of the particle accelerator through a thin (ca 1 µm thick) window of silicon or silicon carbide to probe the electrode or electrolyte of interest in close proximity to the window.

We will present results obtained at CWRU over several years of work with different electrochemical systems and different window materials, demonstrating the capabilities and limitations of in-situ ion beam analysis of electrochemical systems. Most recently, we have developed an experimental technique that allows for real-time evaluation of the radiolysis yield from aqueous solutions subjected to alpha particle radiation.

301. Laser Anemometry for Wind Measurement

David H. Matthiesen, Professor, Materials Science and Engineering, Case Western Reserve University, Cleveland, OH

A LIDAR (LIght Detection And Ranging) system that was capable of measuring wind velocities at 30, 50, 90, 120, and 150 m above the nominal water level was temporarily installed at the City of Cleveland’s offshore water intake crib. Previously, a metrology tower was installed on the water intake crib, which is located approximately 3.5 miles offshore, by Green Energy Ohio and The Renaissance Group [1]. The 50 m tower has redundant cup anemometers to measure wind velocities located at 30, 40, and 50 m above the nominal water level. Wind measurements from this met tower were compared to measurements acquired by a ZephIR LIDAR system [2]. The wind velocity measurements at higher elevations were used to develop a better understanding of boundary layer at this offshore location.

302. Semi-Experimental Structures From High-Resolution Infrared Spectroscopy and Quantum Chemical Calculations

Deacon J. Nemchick, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH

To assess the effects of fluorine substitution on the CC bond lengths in 1,4-difluorobutadiene, semi-experimental equilibrium structures (0.001 Å resolution) are sought. The method of obtaining such accurate structures from the rotational structure in high-resolution infrared spectra, from isotopic synthesis, and from quantum chemical calculations is described. Progress toward determining equilibrium structures for the isomers of 1,4-difluorobutadiene and quantum chemical predictions for the structures are reported.

Solid State Chemistry (2)

Organizer: Catherine M. Oertel Oberlin College, Oberlin, OH
Organizer: Cora Lind University of Toledo, Toledo, OH
Presider: Cora Lind University of Toledo, Toledo, OH

Session Overview: Solid-state chemistry is aimed at the synthesis and characterization of advanced materials. Understanding materials' properties based on the structure of materials, and fine-tuning properties through the study of structure-property relationships, ties together diverse areas like nanomaterials, semiconductors, crystal growth and engineering. In this symposium, new materials, synthetic routes and characterization methods will be presented.

303. Building Extended Solids through Sol-Gel Assembly of Phosphide Nanoparticles: A New Class of Aerogels

Keerthi Senevirathne[1], Ronald Tackett[2], Parashu Ram Kharel[2], Gavin Lawes[2], Autumn Burns[3], Mark E. Bussell[3] and **Stephanie L. Brock**[1], (1)Department of Chemistry, Wayne State University, Detroit, MI, (2)Department of Physics and Astronomy, Wayne State University, Detroit, MI, (3)Department of Chemistry, Western Washington University, Bellingham, WA

Sol-gel methods have proven to be an effective strategy to for the assembly of metal oxides, and even carbon, into porous extended structures. Recently, we and others have shown that this method is also applicable to metal chalcogenides, generating a novel class of optically active porous nanostructures based on II-VI and IV-VI semiconductors. In contrast to traditional oxide methods, where gels are built from hydrolysis and condensation of molecular reagents, for our chalcogenide system, gelation is achieved by controlled de-complexation of pre-formed semiconductor nanoparticles. De-complexation is performed by the addition of an oxidant (hv/O_2, hydrogen peroxide, or tetranitromethane) to quantum dots (MQ; M = Cd, Zn, Pb; Q = S, Se, Te) that are capped with thiolate stabilizing ligands. Oxidative loss of ligands leads to nanoparticle assembly into porous wet gels, the structure of which can be retained in the solid state by using supercritical fluid extraction methods. These chalcogenide aerogels have an interconnected network of micro- and mesopores with a high surface area, and also retain the unique quantum-confinement properties of their nanoparticle precursors. In the present work, the application of this approach to the assembly of metal phosphide nanoparticles, including InP (a direct bandgap semiconductor), MnP (a material with long-range magnetic order) and Ni_2P (a hydrodesulfurization catalyst) will be presented. The implications for the mechanism of self-assembly in chalcogenides and phosphides, and the chemical attributes of the interface, will be discussed in light of the physical properties.

304. Synthesis of $A^{II}B^{IV}M_3O_{12}$ Materials Using the Non-Hydrolytic Sol-Gel Method

Tamam Issa Baiz and Cora Lind, Department of Chemistry, The University of Toledo, Toledo, OH

Recently, there has been an increased interest in negative thermal expansion materials (NTE), which shrink upon heating. Materials exhibiting this property have the potential for achieving better control of thermal expansion through the synthesis of composite materials with more desirable expansion coefficients. A popular family of NTE materials is the $A_2M_3O_{12}$ (A=trivalent cation; M=W, Mo) family. Materials in this family usually adopt an orthorhombic structure at high temperature, which exhibits low or negative thermal expansion. In some cases, these materials can undergo a phase transition to a monoclinic structure at low temperature, which exhibits positive thermal expansion. The temperature at which the transition from monoclinic to orthorhombic occurs is highly dependent on the trivalent cation.

Despite the interest in $A_2M_3O_{12}$ materials, little research has been devoted to synthesizing materials containing two aliovalent cations instead of just one or two trivalent cations. The research presented here targets systems where the A site contains two differently charged cations, leading to the synthesis of materials of the type $A^{II}B^{IV}M_3O_{12}$ (M= W, Mo). These materials are prepared using a low temperature route, known as the non-hydrolytic sol-gel method. This allows facile access to both the tungstates and the corresponding molybdates. The expansion behavior of these materials was characterized using variable temperature powder X-ray diffraction data. Preliminary results for the molybdates indicate a phase transition from the monoclinic to the orthorhombic phase at a temperature much higher than that observed with the corresponding tungstates.

305. Structural and Magnetic Properties of Perovskites with Ordering of Both the A-Site and B-Site Cations

Graham King[1], Lora M. Wayman[1], Andrew S. Wills[2] and Patrick M. Woodward[1], (1)Department of Chemistry, The Ohio State University, Columbus, OH, (2)Department of Chemistry, University College London, London, United Kingdom

Over 20 new perovskite compounds which have the unusual combination of rock salt ordering of the B-site cations and a layered ordering of the A-site cations have been prepared. These compounds exhibit a rich variety of interesting structural and magnetic features. Several of the compounds have been found to adopt polar space groups as a result of both types of cation ordering in combination with octahedral tilting. A number of other compounds have been shown by TEM analysis to have complex nanoscale superstructures. The superstructures are the result of a novel type of compositional modulation that extends throughout the sample. A twinning of the octahedral tilt system has been shown to occur at the compositional boundaries. The magnetic properties are also of interest. In $NaLnMnWO_6$ perovskites, the Mn and Ln moments order simultaneously at temperatures ranging from 10-15K. The magnetic structures of three of these compounds have been determined by neutron powder diffraction. Incommensurate ordering of the moments occurs when Ln is magnetic. Two sequential magnetic phase transitions have been observed in $NaTbMnWO_6$. When Mn is replaced by Mg to form $NaLnMgWO_6$ perovskites no ordering of the Ln moments is observed. The interplay between the Mn^{2+} and Ln^{3+} moments in the $NaLnMnWO_6$ compounds is also discussed.

306. The Interplay Between Spin, Orbital and Chemical Order in $Ca_{2-X}La_xMnRuO_6$ Perovskites

Jennifer Rose Soliz and Patrick M. Woodward, Dept. of Chemistry, The Ohio State University, Columbus, OH

Over the years, perovskites have been studied and found to exhibit fascinating properties. In particular, the main goal of this work is to find a perovskite structure that possesses magnetoresistance properties and half-metallic electron transport. New perovskites that have been synthesized and characterized are the $Ca_{2-x}La_xMnRuO_6$ solid solution. This orthorhombic (Pnma) structure has been identified as phase pure samples with compositions of x = 1.2, 1.0, 0.8, 0.6, 0.4, and 0.2. Through the Rietveld refinements from X-ray powder diffraction (XRPD), the lattice parameters suggest that all samples lack the cooperative Jahn-Teller distortion. No cation ordering was found to occur on either the A-site or B-site. This structure has been found to exhibit the $a^-b^+a^-$ octahedral tilt system. The magnetic properties are also of interest. Using a vibrating sample magnetometer (VSM), susceptibility measurements show that all samples have a ferromagnetic-like ordering between 240-300 K, despite the complete lack of long range Mn/Ru order. However, the saturation moments (0.5 – 1.3 μ_B/f.u.) are too small for full ferromagnetic ordering. Interestingly, the electrical conductivity decreases when lanthanum replaces calcium.

307. Metal Oxide Photoelectrodes Prepared Via Atomic Layer Deposition

Thomas Hamann, Department of Chemistry, Michigan State University, East Lansing, MI

A new materials-general synthetic approach for high-area metal oxide photoelectrode architectures was designed and fabricated for dye-sensitized solar cells. The approach makes use of conformal, atomic layer deposition (ALD) and exploits a templating strategy. ALD was also used to create conformal TiO_2 blocking layers on fluorine-doped tin-oxide (FTO) substrates in DSSCs in order to eliminate shunting, as well as an ultrathin alumina layer to passivate surface states. Photovoltaic performance and electron dynamics of DSSCs with the modified photoanodes will be presented.

Plenary Lecture: Professor Daniel G. Nocera of the Massachusetts Institute of Technology

Organizer: Kenneth W. Street The NASA-Glenn Research Center, Cleveland, OH

308. Personalized Energy for 1 (x6 Billion)

Daniel G. Nocera, Department of Chemistry,, Massachusetts Institute of Technology, Cambridge, MA

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Organic Chemistry: New Synthetic Methodologies (2)

Sponsor: ACS Division of Organic Chemistry, Quanta BioDesign, Ltd., Toledo Section of the ACS
Organizer: Suri Iyer University of Cincinnati, Cincinnati, OH
Organizer: Steven J. Sucheck The University of Toledo, Toledo, OH
Presider: Suri S. Iyer University of Cincinnati, Cincinnati, OH

309. Reversal of Enantioselectivity Using Chiral Amino Alcohol Ligands with Multiple Binding Modes

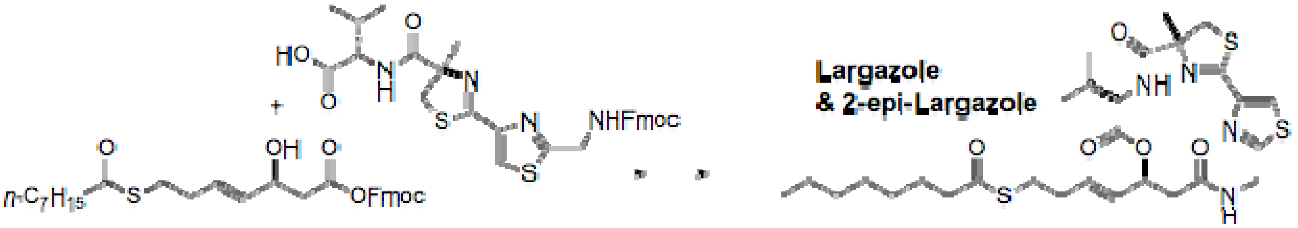
Kyungsoo Oh, Department of Chemistry and Chemical Biology, Indiana University Purdue University Indianapolis, Indianapolis, IN

The development of asymmetric methods that lead to both enantio-enriched products using a single chiral source presents a long-standing interest in organic chemistry. This concept of asymmetric catalysis represents not only a highly attractive synthetic tool using readily available single enantiomeric natural products due to atom-economy issue associated with the preparation of antipode of natural products, but also provides valuable mechanistic information of the reaction processes. Several notable methods have been developed to produce both enantiomeric products by simply changing the reaction parameters without employing the antipode of the chiral source, however the design of effective methods to induce complete reversal of enantioselectivity still remains a significant challenge. On the basis of central role of amino alcohol ligands in the transition metal catalysis, we have devised a new asymmetric approach, which potentially allows access to both enantiomers using different metal binding modes of chiral amino alcohol ligands. Progress towards the realization of high level of reversal of enantioselectivity will be presented.

310. Total Synthesis of Largazole and 2-Epi-Largazole, Potent Anticancer Agents

Bo Wang and Craig Forsyth, Department of Chemistry, The Ohio State University, Columbus, OH

Largazole is a cyclic depsipeptide isolated from a cyanobacterium collected in Key Largo, Florida, by Leusch and co-workers. Its structure and remarkably selective anticancer activities were reported in early 2008. Since then, about ten total syntheses of largazole have been reported in the primary literature. All of these largely employ conventional methodology for peptide bond formation. The OSU synthetic approach is unique in that it employs the application of a novel synthetic strategy that highlights the unique acyl donor activity of nucleophilic heterocyclic carbene intermediates for the facile assembly of the largazole architecture. The scope and limitations of this methodology are illustrated in the ultimate total syntheses of largazole and 2-epi-largazole, both of which have similar levels of anti-proliferative activities.



311. Designing Greener Organic Syntheses Using High Speed Ball Milling (HSBM)

William C. Shearouse and James Mack, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Recently there has been a strong push to minimize waste in the chemical industry. This has triggered a considerable amount of research in greener methodology in organic synthesis. Our research employs High Speed Ball Milling (HSBM) to significantly reduce solvent waste from organic reactions. Where solvents have been used in traditional synthetic methods to achieve homogeneity, HSBM uses mechanical energy to breakdown reagents into small enough particles to the extent where a homogenous mixture is attained. Subsequent collisions of the ball bearing with the walls of the reaction vial result in chemical reactions. One specific class of organic reactions, multi component reactions, has proven to be valuable to many different chemical industries including pharmaceuticals, dyes, conducting polymers, and agrochemicals. This research aims to understand the processes by which multi-component reactions take place under solvent-free, HSBM conditions. More specifically, the Gewald reaction, a multi-component reaction will be discussed. The Gewald reaction involves the reaction of a carbonyl species with an activated nitrile and elemental sulfur in the presence of an amine base. Methods that use a solvent for this reaction make use of long reaction times and tedious reaction methods. HSBM utilizes a one-pot, one-step method while simultaneously producing faster reaction rates in appreciable yields.

312. Twisted and Nonplanar Pincer Complexes: Structures and Catalysis

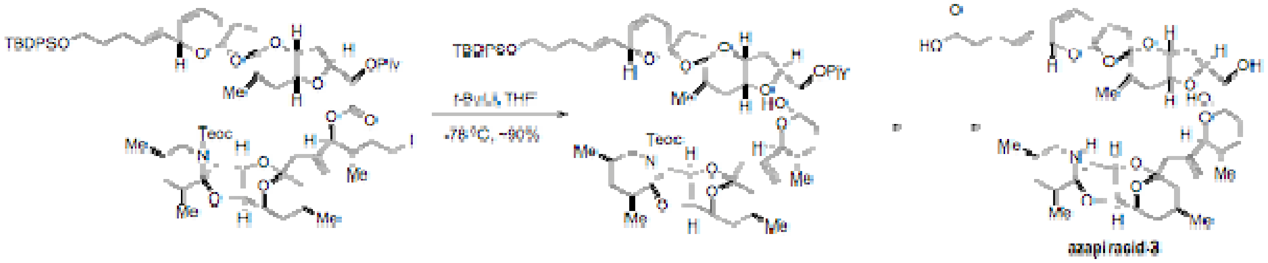
John D. Protasiewicz, Department of Chemistry, Case Western Reserve University, Cleveland, OH

Pincer complexes have become the center of much attention, as they often display great stability and are useful in many applications. We have been exploring a new subset of pincer ligands that are constructed upon a meta-terphenyl framework and having the general form 2,6-(2-D-E-C6H4)2C6H3, where E = CH, CH2 or O, and D = R2P, R2N, and RN. This presentation will highlight palladium, nickel, and iridium complexes that bear these ligands and offer some comparisons to related pincer complexes, as well offer results of studies of their catalytic proficiency in various reactions.

313. The Total Synthesis of Azaspiracid-3

Yue Ding, Jianyan Xu, Feng Zhou, Zhigao Zhang and Craig Forsyth, Department of Chemistry, The Ohio State University, Columbus, OH

The azaspiracids are neurotoxins that accumulate in some shellfish that are consumed by people. These toxins cause acute illness and are suspected of leading to chronic neurological and oncological disease states. Total synthesis efforts have contributed to the structural definition of the azaspiracids, to their environmental detection, and further biological evaluation. Total syntheses of azaspiracid natural products have been reported by the Nicolauo research group, while the Evans group has demonstrated a total synthesis of the non-natural enantiomer of azaspiracid-1. Each of these remarkable synthetic efforts feature low-yielding late stage sequences involving formation of the C20-C21 bonds and subsequent transformations to establish the proper connectivity and functionalization. In contrast, the OSU synthesis of azaspiracid-3 features an efficient convergent coupling of C1-C21 and C22-C40 fragments via an intramolecular Barbier process. Highlights of this unique total synthesis effort will be presented.



314. Palladium Catalyzed Homocoupling of Indole and Aryl Boronic Acids

Jason M. Belitsky, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH

Palladium catalyzed homocoupling of aryl boronic acids has been less widely explored than their cross-coupling with aryl halides––the Suzuki-Miyaura reaction––but with so many aryl and heteroaryl boronic acids now commercially available, homocoupling of these often low cost reagents could become a method of choice for symmetrical biaryl synthesis. A serendipitous result in an attempted cross-coupling of indoles has led us to develop a boronic acid homocoupling reaction that proceeds under very mild conditions (air, water, room temperature). We will describe the development of our method, the role of tosyl chloride as a promoter for certain substrates, and applications of the reaction to the synthesis of indole oligomers related to the human pigment eumelanin.

315. Tethered Lewis Acid-Lewis Base Asymmetric Bifunctional Catalysis: Reaction Rate Acceleration and a New Catalytic Aldehyde Olefination Reaction

Yun-Ming Lin, Ph.D., Department of Chemistry, University of Toledo, Toledo, OH

The allure of emulating enzymatic catalysis by using Lewis acid-Lewis base (LA*—LB*) bifunctional catalysts in asymmetric catalysis has attracted much attention. Recently, we have developed a new family of tethered Lewis acid-Lewis base bifunctional catalysts based on a novel mixed ligand, readily synthesized by covalently attaching quinine to a salen ligand. We have discovered a remarkably active, tethered LA*—LB* bifunctional catalyst that rapidly promotes the enantioselective [2+2] cycloaddition reaction between ketene and aldehydes. The LA*—LB* bifunctional catalyst, a quinine tethered metallosalen complex (5 mol%), catalyzes the [2+2] cycloaddition reaction to produce the C4-substituted beta-lactones from aliphatic/aromatic aldehydes in high isolated yields (71%—97%) and in uniformly >99% ee. The dramatic rate acceleration, the hallmark of cooperative intramolecular bifunctional catalysis, is achieved for the first time for the catalytic, highly enantioselective [2+2] cycloaddition reaction between aldehydes and unsubstituted ketene. In this presentation, we will also describe a new catalytic aldehyde olefination reaction discovered in our laboratory.

Morley Award Symposium

Sponsor: The Cleveland Section of the American Chemical Society
Organizer: Malcolm H. Chisholm The Ohio State University, Columbus, OH
Organizer: Kenneth W. Street The NASA-Glenn Research Center, Cleveland, OH
Presider: Malcolm H. Chisholm The Ohio State University, Columbus, OH
Presider: Kenneth W. Street The NASA-Glenn Research Center, Cleveland, OH

Session Overview: This annual award, sponsored by the Cleveland Section of the ACS, recognizing significant contributions to chemistry through achievements in research, teaching, engineering, research administration and public service, outstanding service to humanity, or to industrial progress in the region.

316. Using Electronic Spectroscopy to Probe Reactive Chemical Intermediates

Terry A. Miller, Department of Chemistry, The Ohio State University, Columbus, OH
Gas phase chemical reactions, such as occur in atmospheric chemistry, combustion, plasma processing, etc. are of great importance to our economy and society. These reactions are typically very complex involving up to 1000's of elementary steps with a corresponding number of reactive chemical intermediates. Spectroscopic diagnostics, based upon well analyzed and well understood spectra of the intermediates, are crucial for monitoring such reactions and unraveling their mechanisms. These spectral analyses often benefit from the guidance provided by quantum chemical calculations of electronic structure and conversely the molecular parameters,

experimentally determined from the spectra, serve as "gold standards" for benchmarking such calculations. Such standards are especially valuable for reactive intermediates whose electronic or geometric structure is particularly complex because of electron-spin interactions, Jahn-Teller effects or other vibronic interactions, hindered internal motions, large molecular size and weight, etc. The organic alkoxy, RO·, and peroxy, RO_2·, (R=alkyl group) free radicals are excellent examples of reactive intermediates involved in the oxidation of organic molecules. The talk will focus on our recent spectroscopic characterization of these radicals. These experiments have been carried out at room temperature obtaining sufficient resolution to distinguish among different isomers, conformers, and isotopologues of the same chemical species. Higher resolution, mostly rotationally resolved, electronic spectra have been observed for radicals jet-cooled to between 1-20K. The techniques of laser induced fluorescence, stimulated emission pumping, and cavity ringdown spectroscopy have been utilized. Selected spectra, their analysis, and the molecular information resulting therefrom will be discussed.

317. Theoretical Studies of the Spectroscopy of Radicals From Kr-OH to CH3O2

Anne B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH

In this talk the outcomes of two projects that we have undertaken in collaboration with Professor Terry Miller’s group at Ohio State will be discussed. The first involves mapping out the electronic spectroscopy of rare gas atoms (Ne, Ar and Kr) with OH and SH. Interestingly, in the case of the SH complexes, the presence of the rare gas atom increases in the excited state lifetime of SH in its ground vibrational state from less than 3 ns up to more than 800 ns. This work also led us to an exploration of the potential surfaces for the more weakly bound complexes in this series, specifically Ne.OH, which is surprisingly anisotropic. This anisotropy made assignment of the intermolecular vibrational modes that were accessed in the spectra more challenging than one would have anticipated for such an apparently simple system. The second part of this talk will focus on a collaborative study that focused on understanding the unexpected band structure in the A-X transitions in CH_3O_2 and CD_3O_2. Interestingly much of the observed structure could be analyzed in terms of a one-dimensional hindered rotor model in which coupling between the large amplitude vibration and the rotation about the heavy-atom axis was taken into account. In both sets of systems, the combination of experiment, theory and computation led to a much simpler physical picture of the overall vibrational dynamics than could have been inferred from the initial observation.

318. Molecular Secrets From High Resolution Spectroscopy In the Gas Phase

David Pratt, Professor of Chemistry, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA

This talk will describe several applications of high resolution spectroscopy techniques to both structural and dynamical problems in chemistry, revealing many molecular “secrets” for the first time. These include studies of the geometries of large molecules and how they change when they absorb UV light, elucidation of the intermolecular potential energy surfaces of a wide variety of van der Waals and hydrogen bonded complexes involving water, and the direct observation, in the frequency domain, of several dynamical processes including tunneling, solvent reorganization, and level mixing via axis tilting, as well as IVR, ISC, and vibrational predissociation. Recent studies of such spectra in the presence of electric fields (the Stark effect) also will be described.

319. The Adiabatic Approximation as a Diagnostic Tool for Torsion-Vibration Dynamics

David Perry, Professor of Chemistry, Department of Chemistry, University of Akron, Akron, OH

The adiabatic separation of large-amplitude torsional motion from small amplitude vibrations is applied as an aid in interpreting the results of fully coupled quantum calculations on a model methanol Hamiltonian. Comparison is made with prior work on nitromethane (D. Cavagnat, L. Lespade, J. Chem. Phys. 106 (1997) 7946). Even though the torsional potentials are very different, both molecules show a transition from adiabatic to diabatic behavior when the CH stretch is excited to $v_{CH}=4$ or higher. This transition is promoted by the normal mode to local mode transition, and the relevant adiabatic and diabatic effective torsional potentials are determined by the torsion-vibration coupling. The torsion-vibration couplings in the four overtone manifolds considered (methanol OH, CH, nitromethane CH, and hydrogen peroxide OH) are large, reaching 265 - 500 cm^{-1} by $v_{XH}=6$, and are of generally similar magnitude. The largest torsion-vibration couplings involve the first Fourier term in the torsional angle ($\cos\gamma$ for the CH stretch in methanol and the OH stretch in HOOH) whereas higher Fourier terms ($\cos 2\gamma$ in nitromethane and $\cos 3\gamma$ for the OH stretch of methanol) result in somewhat weaker coupling. Nonadiabatic matrix elements in methanol couple the torsional and vibrational energies and they exhibit a slow fall-off with coupling order.

Analytical Chemistry (2)

Organizer: John F. Turner Cleveland State University, Cleveland, OH
Organizer: Rebecca Whelan Oberlin College, Oberlin, OH
Presider: Rebecca Whelan Oberlin College, Oberlin, OH

320. A Novel Analytical Method to Determine Crystalline and Amorphous Content in Drugs by Dielectric Thermal Analysis

Manik Pavan Kumar Maheswaram, BSPS[1], Alan Riga, Dr. [1] and K.S. Alexander, Dr. [2], (1)Department of Chemistry, Cleveland State University, Cleveland, OH, (2)College Of Pharmacy, The University of Toledo, Toledo, OH

Differential Scanning Calorimetry (DSC) and Dielectric Analysis (DEA) can easily differentiate morphological and thermodynamic transitions in drugs as well as their crystalline-amorphous content. The DSC crystalline content is based on the melting endotherm of the drug and its ability to recrystallize. The content is determined from a number of heat and cooling cycles to evaluate the drugs ability to recrystallize. The DEA electrical conductivity is repeatable and differentiates the solid crystalline low conductivity level and the high conductivity amorphous liquid. The DSC sets the analytical transition range and the DEA conductivity establishes the content. The DEA employs a standard heating rate, sample size with a gold ceramic interdigitated electrode. The DSC results are compared to the DEA conductivity amorphous and crystalline content identified below the DSC melting temperature for the standard drugs. The Active Pharmacy Ingredients (APIs) include Acetanilide, Acetophenetidin, Sulfapyridine, and Caffeine, Aspirin, and Mefenamic Acid. There was a good agreement between the DSC crystalline melting and recrystallization, the solid state DEA conductivity method and the relevant microscopic determination. The amorphous and crystalline content of the APIs is clearly and repeatably determined in the DSC or DEA cyclic heating and cooling of the drug. The transition from crystalline solid to liquid amorphous drug was accompanied by a conductivity change from ca.10^{-1}pS/cm to 10^{7}pS/cm. Reheating the sample API produced a decrease in crystalline content resulting in a 90% decrease for caffeine and an 18 % decrease for acetanilide.

321. Ionic Liquids and Their Applications as Gas Sensing Materials

Xiangqun Zeng[1], Kuangyu Hou[1], Lei Yu[1], Xiaoxia Jin[1], Yue Huang[2] and Andrew Mason[3], (1)Department of Chemistry, Oakland University, Rochester, MI, (2)Department of Electrical Engineering, Michigan State University, East Lansing, MI, (3)Department of Electrical Engineering, Michigan State University, East Lansing

Ionic Liquids and Their Applications as Gas Sensing Materials Xiangqun Zeng1, Kuangyu Hou1, Lei Yu1, Xiaoxia Jin, Yue Huang2, Andrew Mason2 1Department of Chemistry, Oakland University, Rochester, MI 48309, USA 2Department of Electrical Engineering , Michigan State Univ. East Lansing, MI 48824 , USA Gas sensors are of increasing interests due to their various applications. Ionic liquids (ILs) with their distinctive properties are potential new materials for gas detections. Our studies show that the existence and the strength of the interactions between IL and gas analytes are

dictated by the structures of the ILs and the gas analytes. Recently, a unique and innovative sensor design based on IL and conductive polymer (CP) composites has been validated in our lab. CPs are often regarded as polyions after they are doped. Thus, they provide an excellent substrate for IL immobilization. In this presentation, we will show examples that the absorption of analytes and the redox behavior of the electroactive analytes in the IL can be simultaneously measured by Electrochemical and Quartz Crystal Microbalance transducers. This significant advantage provides simultaneous determination of two properties of the target analyte [sorption/partition interactions with the IL and analyte redox properties] in real-time. These complementary data can cross-validate the measurement results, add selectivity, and significantly increase the accuracy for the detection. We will also discuss an innovative coating method that immobilizes IL on the conductive polymer (CP) template that significantly enhances the IL based gas sensor sensitivity, stability and specificity.

322. Polyvinyl Ferrocene and Its Applications as Gas Sensing Materials

Kuang-Yu Hou and Xiangqun Zeng, Department of Chemistry, Oakland University, Rochester, MI

Recent work in our lab has shown that conducting polymer and ionic liquid composite show excellent gas sensing properties than either material alone. In this presentation, we systematically studied conducting polymer polyvinyl ferreocene properties such as redox states, film thickness, post-treatment and their effects for gas sensing properties by using quartz crystal microbalance transducers. Additionally, we will discuss how PVF redox states affect the final PVF-IL composite gas sensing properties. The ATR-FTIR spectroscopic studies were used to understand the specific molecular interactions, the strength of the interaction in the various PVF films and PVF-IL composites with gas analyte (Ethanol, Dichloromethane, Benzene, 37% Formaldehyde, Methane and Natural Gas). Our studies showed that the PVF oxidation state which was obtained by further redox cycling in 0.1M $NaClO_4$ gave highest sensitivity for 37% Formaldehyde because of the reconfiguration of polymer matrix. The sensitivity of PVF was also significantly increased by IL immobilization. The strength of ion/molecular interaction between IL and each gas analyte depended on the anion structure of IL. The current detection limit for polarity index (>1) gas analyte was as low as about 1% at room temperature. Among the four IL tests (BmiCs, P_{6666}Cs, $P_{666,14}$Ms and $P_{666,14}$ $PrSO_3$), BmiCs showed the highest sensitivities after immobilization in treated PVF oxidation state. The diverse set of PVF redox states and PVF-IL composites allowed the development of sensor array to generate selective response of analyte mixtures due to structural difference and intermolecular interaction for pattern-recognition.

323. Profiling Complexity and Diversity of Secondary Metabolites in Solanum Trichomes Based On Multiplexed Collision Induced Dissociation Combined with LC/TOF MS

Feng Shi, Department of chemistry, Michigan State University, East Lansing, MI and A. Daniel Jones, Department of chemistry and Department of Biochemistry and Molecular Biology, Michigan State University, East Lansing, MI

Glandular trichomes of tomato species secrete a diverse class of secondary metabolites that accumulate on the leaf surface. Knowledge of biosynthesis of major component acylsugars will provide information for manipulation of metabolite production and thus for increment of insect resistance in tomato and other crops. Multiplexed CID coupled with LC/MS is reported here as a powerful tool for nontargeted acylsugars identification, which has capability to generate spectra with and without fragments in a single analysis. The slopes of breakdown curves of characteristic ions generated by multiple CID assist to classify the untargeted metabolites. The cycling of five potentials in multiple CID avoids the need of optimization of CID potentials for various metabolites and extends the dynamic range for abundant metabolites under higher CID voltage since the signal can be decreased by collision induced dissociation. This method successfully identified complex and variety of acylsugars in `Solanum` trichomes. The majority of acylsugars in LA0716 (`Solanum pennellii`) trichomes are acylglucoses containing three fatty acid substituents, Multiplexed CID analysis yielded fragmentation patterns suggestive that acylsugars from accession LA1522 are largely sucrose triesters with all three fatty acids on the glucopyranose unit, while for M82, two fatty acid chains reside on the glucopyranose unit, with one on the fructofuranose unit. Accession LA1777 yielded tri- and tetra-esters of sucrose, with the latter having at least one fatty acid on the fructofuranose unit. Identification of acylsugars in these wild type species by multiplexed CID assists the plant breeders to discover the gene functions.

324. A Reverse Micellular Lipid in the Plasma of the Endangered White-Winged Wood Duck Infected with Avium Tuberculosis

Jody M. Modarelli, Jennifer Razek, Heather Lucas, Karly Tarase, Bryan Kinches, Claire McCarthy, John Marshall, Ryan Williams and Eddie Gisemba, Department of Chemistry, Hiram College, Hiram, OH

The population of the native Asian White Winged Wood Duck (WWWD) is declining at a rapid rate, resulting in their listing on the endangered species list. One reason for their disappearance is Mycobacterium Avium Tuberculosis (TB), a common air, soil and water bacterium infecting 96% of captive WWWD in the US. Avium TB is highly resistant to treatment by antibiotics due to lipids contained in the bacterial envelope. The plasma from 9 ducks housed in a soil-free, TB-free environment at the Hiram College Field Station, 44 ducks housed in a TB-infested environment at the North Carolina Zoo and 5 North Carolina ducks that died of TB, was extracted, separated by TLC and run by LCMS to identify unique lipids. Our initial findings indicate that a phospholipid at m/z 715 was elevated in both the TB & TB-environment samples and that this phospholipid forms a reverse micellular vesicle. The hydrophobic tails of a reverse micelle could be acting as an impermeable barrier protecting the bacteria from degradation and act as a vector for housing peptides that are otherwise unstable in aqueous an environment. The ultimate goal of this research project is to develop a test that will detect early-stage avium TB leading to a better treatment plan and a more promising initial prognosis allowing zoos across the country to monitor waterfowl coming into the states for TB. Our findings could also help the understanding of TB progression in other organisms and may also be useful in other fields of medical research.

325. Preliminary Evaluation of Zosteric Acid for Preventing the Attachment of Quagga Mussels

Sonal Purohit[1], Jeffrey Ram[1], Bi-min Zhang Newby[2] and **Teresa Cutright**[3], (1)Immunology & Microbiology, Wayne State University, Detroit, MI, (2)Chemical and Biomolecular Engineering, The University of Akron, Akron, OH, (3)Dept Civil Engineering, University of Akron, Akron, OH

Mussels, such as Quagga and Zebra, attach to many aquatic man made structures and have been creating an economic burden in North America for almost two decades. Prevention or reduction of the attachment of these Mussels with environmentally friendly approaches is needed. In this study, we evaluate the effectiveness of Zosteric acid, a natural product antifoulant found in eelgrass Zostera Marina and has shown the ability to prevent the attachment of some bacteria and barnacles, on inhibiting the attachment of Quagga Mussels. Animals were exposed to water containing 0, 0.5, 1 or 2 g/L zosteric acid and their attachment to the container was tracked with time. The results show that Zosteric acid was not effective at detaching animals that had pre-attached to the vial, but it exhibited some effectiveness in preventing Quagga Mussels attachment for a short period of time. At low concentrations (≤ 0.2 g/L), zosteric acid was only effective for the first day. As the zosteric acid dose increased (0.5 g/L, 1 g/L and 2 g/L), prevention of attachment was found to last longer, and with a 2 g/L of Zosteric acid, no attachment of Mussels was observed within the first three days and only 20% of the Mussels were found to attach in day 4. Conversely, animals in either control (no zosteric acid) or tris solutions (another control) had reattached within one day.

326. Determination of Triclocarban in Aqueous Matrices by Stir Bar Sorptive Extraction-Liquid Desorption/Liquid Chromatography Tandem Mass Spectrometry

Dustin R. Klein and Melissa M. Schultz, Department of Chemistry, The College of Wooster, Wooster, OH

Triclocarban (TCC) is an antimicrobial and antibacterial agent found in personal care products and is a prevalent wastewater contaminant. Despite widespread use, few analytical methods exist to detect TCC in environmental matrices, thus little is known about its distribution and fate in the environment. A quantitative method was developed for the analysis of TCC in groundwater and wastewater using stir bar sorptive extraction and liquid desorption (SBSE-LD) followed by liquid chromatography tandem mass spectrometry by means of an electrospray interface. The conditions and parameters for the SBSE-LD using a polydimethylsiloxane coated stir bar were optimized and included selecting the desorption solvent and extraction time. The most efficient extraction of TCC from aqueous matrices included an equilibration time of 24 h with methanol as the back-extraction solvent. Recoveries were on the order of 80%. The extracts were then separated by reverse-phase chromatography and quantitated by mass spectrometry using multiple-reaction-monitoring. The validated method was applied to a set of municipal wastewater samples collected from plants in and around the Cleveland area.

327. Aldehydes Photolysis with OH Radical Under High NOx

Heber J. Chacon-Madrid and Neil M. Donahue, Chemistry Department, Carnegie Mellon University, Pittsburgh, PA

It is known that smaller aldehydes such as ethanal and propanal react with OH radicals under high NOx conditions to form their n-1 aldehyde, meaning formaldehyde and ethanal respectively. Less is known for bigger aldehydes, and nothing about the molar yield formation of their respective n-1 aldehydes. Three aldehydes are explored, n-tridecanal, n-octanal and n-pentanal. Their molar yields are determined using a 12 m^3 Smog Chamber, and monitoring the different species with a PTRMS instrument. The formation of the n-2 and n-3 aldehydes is studied as well. The molar yields are used to interpret their contribution to SOA (Secondary Organic Aerosol) formation. SOA yields are obtained for some of the aldehydes studied. A correlation between molar yield and SOA yield is done to better understand their SOA contribution.

Computational Chemistry (4)

Organizer: Jane S. Murray Cleveland State University, Fairview Park, OH
Organizer: Peter Politzer Cleveland State University, Fairview Park, OH
Presider: Peter Politzer Cleveland State University, Fairview Park, OH
Presider: Jane S. Murray Cleveland State University, Fairview Park, OH

Session Overview: Acknowledgements: We greatly appreciate the support provided by the U. S. Office of Naval Research and the Computers in Chemistry Division of the American Chemical Society.

328. Electronic Polarization and Transfer During Chemical Reactions

Alejandro Toro-Labbé and Soledad Gutierrez-Oliva, Faculty of Chemistry, Pontificia Universidad Católica de Chile, Santiago, Chile

The mechanism of chemical reactions can be understood in terms of the reaction force concept that provides the elements to characterize simultaneously the thermodynamics, kinetics and the mechanism of the reaction through a rational fragmentation of the reaction coordinate which define reaction regions featuring specific and unique characteristics. It has been observed in different kinds of chemical reactions that in these reaction regions specific interactions among atoms or fragments of the interacting molecules are activated and/or inhibited, such that these interactions drive the changes occurring in the molecular structures and electronic densities when going from the reactants to the products of the reaction. Within this context, the reaction electronic flux (REF) has been recently introduced with the aim of characterizing the specific features observed in the electronic reordering that take place during the reaction. The REF is the negative of the chemical potential gradient. Within the framework of the reaction force analysis, the REF is used to identify the regions along the reaction coordinate where electronic polarization and/or transfer are driving the reaction. For a physical interpretation, the REF is partitioned into intra and intermolecular contributions, characterized by polarization effects on each reactant and a net charge transfer between them. In this work results of application of the REF for rationalizing the mechanism of different reactions are presented.

329. Characterizing Complexes with F-Li$^+$-F Lithium Bonds: Structures, Binding Energies, and Spin-Spin Coupling Constants

Janet E. Del Bene, Ph.D., Chemistry, Youngstown State University, Youngstown, OH

Ab initio MP2/aug-cc-pVTZ calculations have been performed to determine the structures and binding energies of complexes with F-Li$^+$-F bonds formed from the fluorine bases LiF, CH_3F, HF, ClF, and FF. There is only a single minimum across the Li$^+$ transfer coordinate, and in each series, the lithiated homodimer is stabilized by a symmetric F...Li$^+$...F bond. Complexes formed from LiF, CH_3F, and HF have similar structures, with linear F-Li$^+$-F bonds and a head-to-tail alignment of the F-Li$^+$ bond dipole with the dipole moment vector of the base. In each series with a given acid, the binding energy decreases as the difference between the lithium ion affinities increases. EOM-CCSD coupling constants ^{1}J(F-Li), ^{1li}J(Li-F) and ^{2li}J(F-F) have also been evaluated. In complexes with essentially linear bonds, ^{2li}J(F-F) values are small and positive, and increase quadratically as the F-F distance decreases. ^{1li}J(Li-F) and ^{1}J(F-Li) also vary systematically with distance. Comparisons are made between structural, energetic, and coupling constant properties of these complexes and corresponding complexes stabilized by F-H$^+$-F hydrogen bonds.

330. Investigations On the Origins and Nature of Halogen Bonding by Ab Initio Methods

Kevin E. Riley, PhD, Chemistry, University of Puerto Rico, San Juan, PR

Halogen bonding is a unique type of noncovalent binding phenomenon in which a halogen atom interacts attractively with an electronegative atom such as oxygen or nitrogen. These types of interactions have been the subject of many recent investigations because of their potential in the development of new materials and pharmaceutical compounds. Here the phenomenon of halogen bonding is investigated using ab initio calculations on the halomethane-formaldehyde complexes as well as the, fluorine substituted, dimers, where the halogen bonding halogens ( ) are chlorine, bromine, and iodine. Coupled cluster (CCSD(T)/aug-cc-pVTZ) calculations indicate that the binding energies for these type of interactions lie in the range between -1.05 kcal/mol ( ) and -3.72 kcal/mol ( ). One of the most important findings in this study is that, according to symmetry adapted perturbation theory (SAPT) analyses, halogen bonds are largely dependent on both electrostatic and dispersion type interactions. As the halogen atom involved in halogen bonding becomes larger the interaction strength for this type of interaction also gets larger and, interestingly, more electrostatic (and less dispersive) in character. Halogen bonding interactions also become stronger and more electrostatic upon substitution of (the very electronegative) fluorines onto the halomethane molecule. Results of ab initio studies (including SAPT) on variously substituted bromobenzene…acetone complexes are also discussed. It was found that replacement of ring hydrogens in these systems has dramatic effects upon the interaction strengths of the resulting complexes, which have interaction energies between -1.80 kcal/mol and -7.11 kcal/mol.

331. Developing of Isothiazole Analogs as Potent MEK1 Inhibitors by Molecular Modelling Studies

Parthasarathy Tigulla, active researcher, Department of Chemistry, Osmania University, Hyderabad, India

Developing of Isothiazole analogs as Potent MEK1 Inhibitors by Molecular Modelling Studies B. Ashok Kumar and T. Parthasarathy* Dept of Chemistry, Nizam Collage, Osmania University, Hyderabad – 500 001, INDIA. Mitogen activated protein kinase (MEK), a dual specificity kinase, has a central role in extracellular signal regulatory kinase (ERK) pathway in regulating cell growth and survival, differentiation, and angiogenesis. The MEK and ERK are frequently dysregulated in human cancers. The over expression and activation of these enzymes were associated with various human cancers including kidney, breast, colon and oral carcinomas, leukemia and glial neoplasmas. The MEK 1/2 are the only enzymes known to activate ERK 1/2 and it is believed that their inhibition might be useful in controlling the growth of cancer cells. 31 Isothiazole analogs were selected as kinase inhibitors and docking studies were performed on human MEK 1. The docking studies reveal that substitutions on amidines, of small alkyl groups and alkyl groups with hydrophilic groups (OH) are favoured and improve the activity substantially. Further, it was also found that ortho substitution on phenyl ring improves the potency by 8 to 20 fold. Ortho substitution on 5-phenylamino group coupled with hydroxyalkyl- carboxyamidino substitution further enhances the potency by 6-fold. E-mail : sarathychem@gmail.com

332. A New QSAR Method for the Prediction of the Absorption Isotherms of Amines

Aurelie Goulon[1], Abdelaziz Faraj[1], Marc Jacquin[2] and Fabien Porcheron[2], (1)Applied mathematics, IFP, Rueil_Malmaison, France, (2)IFP, Solaize

To reduce CO2 emission into the atmosphere, one solution consists in processing the industrial fumes by washing them with a chemical solvent which is generally an aqueous solution of amine. However, an important work is still necessary to prospect for new solvents, requiring a lower amount of energy in the regeneration stage, good kinetics, and a low degradation. Since the number of available amines is important, it is advantageous to resort to QSAR methods, to find a relation between the structures of the amines and their activities.

We present a statistical learning modelling method – called `graph machines` – where molecules are considered as structured data and represented by graphs. In a classical QSAR approach, molecules are generally described using vectors composed of a large set of molecular descriptors. In this work, an alternate approach is used as we suppose that all the required information is contained within the structure of the molecule. Since no molecular descriptors are used, the collection, computation and selection of these descriptors, which is often a major issue in QSAR applications is no longer required.

For each individual of the data set, a mathematical function is built, which structure reflects the structure of the molecule under consideration. This function is the combination of identical parameterized functions which are adjusted during training. Model selection is then performed by cross-validation and prediction.

This method was used to model properties of amines, e.g. their absorption isotherms. We present the results obtained by this new approach for modelling these properties.

Energy Storage and Energy Conversion: Aqueous Battery Systems

Organizer: Cristian Fierro Ovonic Battery, Troy, MI
Organizer: Irina Serebrennikova Energizer, Westlake, OH
Presider: Cristian Fierro Energy Conversion Devices, Troy, MI

Session Overview: This symposium will provide an opportunity to discuss recent progress towards the development and advances of aqueous battery systems. The symposium will focus on both basic and applied research findings that have led to improved materials and energy storage devices.

333. Chemistries and Technical Issues of Flow Redox Batteries for Large Scale Energy Storage

Robert F. Savinell, Robert Armstrong and Jeffrey Justus, Chemical Engineering, Case Western Reserve University, Cleveland, OH

Flow redox battery systems are a hybrid between fuel cell-type technology and battery technology, and are based on simple reactant and product species dissolved in a working fluid. The advantages of redox flow batteries include: independent sizing of energy storage capacity and power capacity making for modular designs; moderate costs; transportability so systems, or even just the reactant solutions, can be located to meet demands; and flexibility in that full and partial discharges should not impact performance or life. Research and development on redox batteries, although intense about 30 years ago, has been reinvigorated recently due to the interests in storing intermittent renewable energy sources like wind and solar, and for increasing efficiency of power in the grid. This talk will summarize some of the chemistries examined over the years and describe performance and technical issues reported on flow redox batteries.

334. Phase Stability and Crystal Structure of NiOOH From First Principles

Anton Van der Ven, Materials Science and Engineering, The University of Michigan, Ann Arbor, MI

Nickel hydroxide compounds are widely used as cathodes in primary and secondary alkaline batteries. Although the general features of Ni-hydroxide-based electrode materials have been characterized over the last century, many of their basic properties remain unknown. Important questions persist about the precise crystal structures of gamma NiOOH and beta NiOOH. In this talk I will describe the results of a first principles investigation of phase stability of nickel hydroxides. Stable crystal structures for beta-NiOOH and gamma-NiOOH are predicted and are characterized by stacking sequences of the NiO2 slabs that maximize primary and secondary hydrogen bonds. The predicted crystal structures provide insight about the capacity limits observed experimentally in nickel-hydroxide based electrodes.

335. Nickel Hydroxide In Nickel Metal Hydride Batteries

Cristian Fierro, **John Koch**, Avi Zallen and Michael Fetcenko, Ovonic Battery Company, Energy Conversion Devices, Troy, MI

Ovonic Battery Company has developed a commercial and proprietary process to produce Dense Spherical Nickel Hydroxide (DSNH) particles, a crucial NiMH battery component which is strategically important to Ovonic's licensees. Ovonic Battery is the only facility producing DSNH in the US.

Ovonic's proprietary production system for the low-cost synthesis of DSNH allows its users to produce superior Ni-MH batteries, in particular for cycle life and high temperature performance. The latter is a critical area for Ni-MH batteries because many battery applications operate at elevated temperatures, including electric vehicles, hybrid electric vehicles, emergency lighting, and stationary power. A variety of DSNH powders, with different Ni/Co/Zn ratios will be presented. The powders were studied by cyclic voltammetry and tested in C-cells. It was found as the amount of co-precipitated cobalt in these powders is increased the oxygen evolution reaction is decreased. This data correlates well with C-cell measurements performed at different temperatures. It was found that high temperature charge efficiency is improved as the amount of co-precipitated cobalt present in these powders is increased.

336. Development of Characterization Methods to Correlate Surfactant Physical Properties with Alkaline Performance

Alex Fensore[1], Andre Sommer, Professor and Director of MM Lab at Miami University[2], John Matias[1] and Dawn Freeman[1], (1)Energizer, Westlake, OH, (2)Chemistry & Biochemistry, Miami University of Ohio, Oxford, OH

Surfactants have been used in alkaline anodes to reduce corrosion, increase high rate service, and improve the rheological characteristics of the anode. If the relative affinity of the surfactant for the ZnO discharge product, Zn, and the brass nail could be controlled, Zn corrosion, service, and anode processability could be further optimized.
In order to control the affinity of a surfactant for these anode components, the coverage of surfactant on them must be quantified. Fourier transfer infrared spectroscopy (FTIR) imaging was utilized to map the coverage of different surfactant chemistries on the surface of these anode components. The FTIR imaging technique has been successful in identifying which surfactant chemistries have a higher affinity for each substrate. Electrochemical impedance spectroscopy, contact angle measurements, and other electrochemical tests were also used to characterize the surfactants in relationship to their performance in an alkaline anode.

Energy Storage and Energy Conversion: Lithium Ion Batteries and Supercapacitors

Organizer: Gholam-Abbas Nazri N/a, N/a

Session Overview: This session covers material aspects of advance lithium ion batteries, including recent progress in developing high capacity cathode and anode materials, new developments in electrolytes and additives to improve the safety of lithium cells. The fundamental science of lithium intercalation in layered oxides and graphitic materials, as well as the energetics of olivine phosphate materials will be discussed. The role of electrode engineering to mitigate slow kinetics and provide fast rate electrodes for transportation applications will be reported. Application of various characterization techniques for real-time study of electrodes under electric field control will be addressed.

337. Discussion of the Lithium Deintercalation Mechanism in Carbon-Coated LiFePO4 Nanoparticles

Laurence Croguennec[1], François Weill[1], Magali Maccario[1], Rémi Dedryvère[2], Alain Wattiaux[1], Frédéric Le Cras[3], Danielle Gonbeau[2] and Claude Delmas[1], (1)Icmcb - Cnrs, University of Bordeaux, Pessac, France, (2)Iprem/ECP, Université de Pau et des Pays de l'Adour, Pau, France, (3)Drt/Liten/Dtn/Lce, CEA, Grenoble, France

Since the pioneering work of Padhi et al., who proposed for the first time the use of $LiFePO_4$ as positive electrode in lithium batteries, a huge number of studies were devoted to the optimization of its electrochemical performances and to the study of the lithium deintercalation mechanism. Indeed, as both end member phases ($Li_{1-e}FePO_4$ and $Li_{e'}FePO_4$) are very poor ionic and electronic conductors it is difficult to understand how this material can deintercalate (and then intercalate) lithium ions at very high rates. Here, we will discuss results obtained for electrochemically deintercalated 100 nm $LiFePO_4$ nanoparticles. X-ray photoelectron spectroscopy analyses revealed first a continuous change upon charge and discharge of the Fe^{3+}/Fe^{2+} ratio at the surface of the studied particles, in good agreement with the migration of a reaction front inside the particles but not with the "shrinking-core" model. X-ray diffraction analysis illustrates perfectly the two-phase reaction mechanism occurring during lithium deintercalation. Nevertheless FWHM values clearly did not change significantly, suggesting that as soon as lithium deintercalation is initiated at one point of the crystallite it spreads almost immediately everywhere in the bulk. Transmission electron microscopy data confirms that the “Li_xFePO_4” sample is at any state of charge a mixture of $Li_{1-e}FePO_4$ and $Li_{e'}FePO_4$ crystallites. These results will be compared to others reported in literature and a lithium deintercalation mechanism will be proposed, taking into account transport as well as structural properties.

338. Time-Resolved X-Ray Diffraction Study On Structural Evolution in Olivine Materials for Lithium Rechargeable Battery

Ying Meng and J.L. Jones, Department of Materials Science and Engineering, University of Florida, Gainesville, FL

The olivine structure provides a unique low energy ion pathway for fast diffusion of lithium ions through tunnel structure. The Olivine cathodes , particularly the LiFePO4 has been considered for large format lithium battery for power tools and transportation applications. This study has focused on structural dynamics of olivine cathode materials using real-time x-ray diffraction. The structural modification during lithium insertion-extraction has been studied. The XRD study also has been complemented by theoretical study of olivine cathodes.

339. Design of Aqueous Processed Thick LiFePO4 Composite Electrodes for High Energy Lithium Batteries

Bernard Lestriez[1], Willy Porcher[2], Jouanneau Séverinne[2] and Guyomard Dominique[1], (1)Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 44322 Nantes Cedex 3, France, (2)Laboratoire des Composants pour l'Energie, CEA, LITEN, 38 054 Grenoble Cedex 9, France

This work aims at: giving a fundamental understanding of the formulation of the composite electrode of a lithium battery ; and rationalizing its design to optimize the battery performance. The aqueous processing of $LiFePO_4$-based thick positive composite electrodes for high energy lithium battery is studied. The transposition from the organic (NMP) to the aqueous processing improves safety and cost aspects of the fabrication of the battery. The elaboration of thick electrodes with a high surface capacity (3 mAh per cm²) is an industrial challenge.

In addition to the active material and the conductive agents, an aqueous formulation contains a binder, a thickener which role is to give to the electrode slurry proper flow properties with respect to tape casting, and a surfactant which role is to achieve the dispersion of the hydrophobic conductive agent (carbon black) in aqueous medium. The effect of the molecular structure of the thickener and of the surfactant, and the mechanism by which both operate are investigated here. As thickeners, we compare HPMC and CMC. As surfactants, we compare, an anionic one (SDS), a non ionic one (Triton-X100), and a cationic one (CTAB). Relationships between the electrode slurry state, its rheological properties, the electrode morphology, and its electrochemical performance are studied. This allows to select the more efficient molecules of each type (thickener and surfactant) and to determine their optimal concentration. Experimental protocols and relationships between the active material and conductive agent characteristics for extrapolation of our results to others composite electrode formulations are also proposed.

340. Layered Composite of Graphite Nanoplatelet and Polypyrrole for Supercapacitor Application

Sanjib Biswas and Lawrence T. Drzal, Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI

Graphene, a two dimensional aromatic macromolecule, is found in one of the most abundant elements on earth, graphite. The exceptionally low electrical resistivity of graphene originates from the high degree of aromaticity and the presence of a delocalized π-electron structure. Exfoliated graphene nanoplatelets, developed in the Drzal research group in Michigan State University,

consisting of few layers of graphene are prepared from natural graphite through a simple intercalation and exfoliation process. These nanosheets contain the aromaticity of the graphite basal plane without extensive chemical treatments. The average thickness of these nanosheets can be varied from 3 to 10 nm and the size can be varied from submicron to a lateral dimension as large as 100 µm. With high surface area and superior electrical conductivity this nanomaterial is a potential candidate for supercapacitor electrodes. However, the double layer capacitance of carbon nanomaterials is always less than materials exhibiting psedocapacitance based on faradic charge transfer process. Thus the use of inexpensive conductive polymers as a psedocapacitative material for electrochemical capacitors is increasingly gaining interest owing to their high specific capacitance. However, the electrochemical properties suffer from poor electrical conductivity. Here in this research, aligned compact monolayer of large sized graphene nanoplatelets is integrated in a layer by layer structure with highly fibrous polypyrrole nanowires. The alignment of both the graphene nanoplatelets and the porous conductive polymer exhibits improved ion and electronic conduction resulting in better cyclic voltammetric and charge discharge characteristics for this composite supercapacitor electrode.

341. Customizing Macroporous Fiber-Supported Carbon Nanoarchitectures for Electrical Energy Storage

Debra R. Rolison[1], Jeffrey W. Long[1], Justin Lytle[2], Megan B. Sassin[1], Jean Marie Wallace[3], Anne E. Fischer[3], Amanda J. Barrow[1], Jennifer L. Dysart[1], Christopher N. Chervin[1], Katherine A. Pettigrew[3] and Christopher H. Renninger[1], (1)Code 6170, Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, DC, (2)Pacific Lutheran University, (3)Nova Research, Inc., Alexandria, VA

Combining a three-dimensional, electrically conductive, high-surface-area network with a through-continuous, 3-D porous network presents a versatile design strategy to optimize electrode structures. Carbon aerogels are not optimized electrode structures for a range of energy storage and conversion chemistry because of restricted pore sizes (micropore to small mesopores), a lack of electrochemical functionalities that store faradaic charge, and a surface physicochemical character that poorly supports relevant noble metal catalysts. We overcome the first critical disadvantage by fabricating device-ready carbon nanofoam within carbon-fiber paper. Resorcinol–formaldehyde sol, infused into the voids of commercially available low-density carbon fiber paper, upon gelation, air- (not supercritical) drying, and pyrolysis yields lightweight, mechanically flexible, and electrically conductive sheets of fiber-supported ultraporous carbon. The resulting materials comprise nanoscopic carbon walls that envelop macropores (50–300 nm)—a range of pore sizes that provides ample headspace to support additional functionalities without occluding the void volume of the nanofoam. To customize the carbon fiber-supported nanofoams for specific electrochemical, separation, or catalytic applications, we modify the walls of the nanofoam to incorporate such functionalities as electroactive and ion-conducting polymers, mixed-conducting metal oxides, and specifically adsorbed noble-metal nanoparticles.

342. Synthesis and Optimization of LiNi1/3Co1/3Mn1/3O2

Eric Ligneel, Chemistry, Ohio University, Athens, OH

The most widely used commercial cathode material for lithium-ion batteries is lithiated cobalt oxide, $LiCoO_2$. This layered oxide provides an average voltage of 3.75 vs. lithiated graphite, LiC_6. It is easy to prepare and has a stable electrochemical cycling performance with an acceptable specific capacity, 120-150 mAh/g. However the major problem is the high cost of cobalt, and the limited thermal stability of the electrode at high state of charge.

T. Ohzuku was first to report a new derived cathode material from $LiCoO_2$, which is $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$. This material combines a good energy density (over 200mAh/g), between 2.8V and 4.6V, lower cost, and improved safety characteristics as compared with $LiCoO_2$. It was shown that the substitution of Co by Mn, which is electrochemically inactive in this range of voltage, remains as Mn^{IV} and stabilizes the metal oxide slabs even at high state of charge. $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ has still several disadvantages. First during the synthesis process, there is a facile route for migration of transition metals into lithium sites. This phenomenon decreases the lithium insertion/deinsertion efficiency of the active material. Second, at high potential, the oxygen loss is significant and induces an irreversible capacity loss during cycling.

In this paper, synthesis of $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ by a nitrate decomposition route will be reported. The layered material is optimized by adjusting synthesis parameters, including temperature of synthesis, lithium stoichiometry. We also tried to improve the material structure stability at high voltage by cationic and anionic substitutions and by protecting the material surface through special coating technique.

343. Effect of Combinations of Additives On the Performance of Lithium Ion Batteries

Li Yang[1], Ang Xiao[1], Stuart Santee[1], Brett L. Lucht[1] and Joe Gnanaraj[2], (1)Department of Chemistry, University of Rhode Island, Kingston, RI, (2)Lithion Inc., Pawcatuck, CT

Commercial lithium-ion batteries have excellent performance at room temperature for a few years (3-5). However, the calendar life and thermal stability (> 50 oC) need to be improved for many applications, including electric vehicles. We have conducted an investigation of the effect of thermal stabilizing additives, including dimethyl acetamide, vinylene carbonate, and lithium bis(oxalato) borate, on the performance of lithium ion batteries stored at 70 oC for one month. The reactions of the lithium hexafluorophosphate/carbonate electrolyte, with and without electrolyte additives, with the surface of the electrodes after initial formation cycling have been analyzed via a combination of IR-ATR, XPS, and SEM.

Functional Materials: Carbon & Allotropes

Organizer: Greg M. Swain Michigan State University, East Lansing, MI
Presider: Greg Swain Michigan State University, East Lansing, MI

Session Overview: sp2-bonded carbon electrode materials (e.g., graphite, glassy carbon and carbon fiber) have been utilized in electrochemistry for over five decades now. Even so, there remains much that is incompletely understood about the structure-function relationship of these materials. More recently, new types of carbon electrode materials have begun to be investigated and utilized. These include sp3-bonded materials (e.g., micro and nanocrystalline diamond), mixed sp2/sp3 materials (e.g., diamond-like carbon and tetrahedral amorphous carbons), and advanced sp2-bonded materials (e.g., fullerenes and graphene). Oral and poster presentations are invited that cover both fundamental and applied aspects of these carbons. Relevant topics include: material synthesis; physical, chemical, electronic and electrochemical properties of the materials; chemical modification; and electrochemical applications.

344. Some Properties of Diamond Based Composites to Work in Lunar Dust

Kenneth W. Street, Tribology and Mechanical Components, The NASA-Glenn Research Center, Cleveland, OH and Oleg A. Voronov, Diamond Materials, Inc, Piscataway, NJ

Return to the moon is creating a large number of challenges centered around dust and the abrasive nature of lunar regolith. The lunar environment provides no weathering mechanism to round sharp edges of dust particles. During the Apollo missions to the moon, the dust component of regolith adhered to and scratched surfaces with which it came into contact. In preparing for the return missions we are interested in the development of lightweight materials that are abrasion resistant and can be used for bearings in lunar programs. Abrasive wear is generally low when hardness is high. Diamond is the hardest material known; therefore, diamond-based composites (DBCs) might be well suited for such applications. In this work, we examine some properties of one DBC including its friction coefficients and wear.

The samples of DBC were fabricated from a mixture of diamond powder and mixed fullerenes under high pressure. In such a composite, diamond grains are bonded by the matrix that comprises the new carbon material, Diamonite-B. This material is neither graphite-like, nor diamond-like, but exhibits electrical properties close to graphite and mechanical properties close to diamond. Low sliding friction coefficients and low wear are among them. Diamond based composites may work in lunar dust without lubrication. We compare hardness, electrical conductivity, thermal conductivity, X-Ray spectra, Raman spectra and high resolution electron microscopy images for Diamonite-B with graphite-like and diamond-like materials and composites.

345. Exfoliated Graphite (Graphene) Nanoplatelets: A Path to Multifunctionality for Polymers and Composites

Lawrence T. Drzal, Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI

Nanocomposites composed of polymers reinforced with exfoliated clays and carbon nanotubes are being considered for applications such as interior and exterior accessories for automobiles, structural components for portable electronic devices, and films for food packaging. While most nanocomposite research has focused on exfoliated clay platelets and carbon nanotubes, the same nanoreinforcement concept can be applied to another layered material, graphite, to produce nanoplatelets. Graphite is the stiffest material found in nature (Young's Modulus = 1060 MPa), having a modulus several times that of clay, but also having excellent electrical and thermal conductivity. With the appropriate surface treatment, the exfoliation and dispersion in a thermoset or thermoplastic polymer matrix results in a composite with excellent mechanical, electrical, thermal and barrier properties, opening up many new structural applications as well as non-structural ones where electromagnetic shielding, high thermal conductivity or barrier performance are requirements as well.

The process for preparing exfoliated nanographite platelets will be presented along with the role of platelet size, surface chemistry, and processing. Examples of mechanical, thermal, electrical and barrier properties of exfoliated nanographite platelet reinforced thermoset and thermoplastic polymers will be presented, including modulus, strength, coefficient of thermal expansion, HDT, AC Impedance, thermal conductivity and permeability. The results will be compared and contrasted with the same polymer matrices reinforced with nanoclay, carbon fibers, vapor grown carbon fibers and particulate graphite.

346. Visualizing and Measuring Electrochemical Reactivity of Individual Single-Walled Carbon Nanotubes

Shigeru Amemiya, PhD, Chemistry, University of Pittsburgh, Pittsburgh, PA

Carbon nanotubes have been considered as attractive sources of electrode materials for molecular electronics, sensors, catalysis, and energy conversion and storage. In this presentation, a new application of scanning electrochemical microscopy (SECM) to electrochemical characterization of individual single-walled carbon nanotubes (SWNT) is described. With this scanning probe microscopic technique, a micrometer- or submicrometer-sized ultramicroelectrode is employed as a probe for imaging and mapping surface reactivity of an individual SWNT on an insulating surface. The spatially resolved characterization will enable us to address how a redox reactivity of a SWNT depends on the size, helicity, and defect of the carbon lattice. These effects cannot be studied using an ensemble of SWNTs, which are obtained only as mixtures with different structures and subsequently different conductivities. Moreover, the SECM method does not require the integration of a SWNT into an electrode format by tedious lithography, thereby enabling characterization of pristine SWNTs. A proof-of-principle experiment is demonstrated by employing an ultralong SWNT with >1 mm in length and ~ 1.5 nm in diameter as grown on a silicon oxide surface by chemical vapor deposition. A very fast rate of electron transfer at a SWNT is revealed by numerically simulating fast mass transfer of redox molecules at the nanometer-diameter tube.

347. Layered Composite of Graphite Nanoplatelet and Polypyrrole for Supercapacitor Applications

Sanjib Biwas, Chemical Engineering, Michigan State University, East Lansing, MI

Graphene, a two dimensional aromatic macromolecule, is found in one of the most abundant elements on earth, graphite. The exceptionally low electrical resistivity of graphene originates from the high degree of aromaticity and the presence of a delocalized π-electron structure. Exfoliated graphene nanoplatelets, developed in the Drzal research group in Michigan State University, consisting of few layers of graphene are prepared from natural graphite through a simple intercalation and exfoliation process. These nanosheets contain the aromaticity of the graphite basal plane without extensive chemical treatments. The average thickness of these nanosheets can be varied from 3 to 10 nm and the size can be varied from submicron to a lateral dimension as large as 100 µm. With high surface area and superior electrical conductivity this nanomaterial is a potential candidate for supercapacitor electrodes. However, the double layer capacitance of carbon nanomaterials is always less than materials exhibiting psedocapacitance based on faradic charge transfer process. Thus the use of inexpensive conductive polymers as a psedocapacitative material for electrochemical capacitors is increasingly gaining interest owing to their high specific capacitance. However, the electrochemical properties suffer from poor electrical conductivity. Here in this research, aligned compact monolayer of large sized graphene nanoplatelets is integrated in a layer by layer structure with highly fibrous polypyrrole nanowires. The alignment of both the graphene nanoplatelets and the porous conductive polymer exhibits improved ion and electronic conduction resulting in better cyclic voltammetric and charge discharge characteristics for this composite supercapacitor electrode.

348. Structure and Properties of Nanocrystalline Diamond Deposited From Ar-Rich and H2-Rich Gas Mixtures

Greg Swain, Department of Chemistry, Michigan State University, East Lansing, MI

The microstructural, electrical and electrochemical properties of boron-doped (ultra)-nanocrystalline diamond (UNCD) films deposited from a $CH_4/H_2/Ar$ source gas mixture were compared with those of boron-doped nanocrystalline diamond (NCD) films grown from a conventional CH_4/H_2 source gas mixture. Scanning electron microscopy, visible-Raman spectroscopy and x-ray diffraction analysis were employed to probe the film morphology and microstructure. Conducting-probe atomic force microscopy (CP-AFM) was used to simultaneously map the morphology and electrical conductivity of the two film types. Spatial heterogeneity in the electrical conductivity was observed for both films as each is composed of regions of high electrical conductivity isolated by more insulating regions. The electrochemical properties were evaluated using the redox couples: $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$, methyl viologen, dopamine, and $Fe^{3+/2+}$. Taken together, the results confirm that even though the morphology and microstructure of UNCD and NCD films are distinct, both boron-doped film types exhibit comparable electrical and electrochemical properties.

349. Boron-Doped Polycrystalline Diamond On Flexible Non-Planar Substrates

Jeffrey Halpern, Chemical Engineering, Case Western Reserve University, Cleveland, OH and Heidi B. Martin, Case Western Reserve University, Cleveland, OH

Conductive diamond has potential advantages for `in vivo` electrical recording, stimulation, and electrochemistry because of chemical stability, higher signal-to-noise ratio, and reduced biological fouling relative to traditional electrode materials. However, to confirm this, a diamond electrode must be designed to withstand movements of a live, freely-behaving animal. The fabrication of first and second generation “flexible” diamond electrodes for `in vivo` experiments will be demonstrated.

For the first generation electrode, boron-doped microcrystalline diamond was deposited onto tungsten wire substrates by hot-filament CVD. Each wire was pre-shaped and masked for selective growth on only 2-3 mm of the wire. After diamond growth, the uncoated region was removed and the intact diamond-coated section attached to a stainless steel electrical lead with conductive epoxy.

Our second generation "flexible" diamond electrode has been fabricated by selectively growing diamond on the ends of masked rhenium alloy wires. The uncoated regions remained "flexible" even at the interface of uncoated metal and diamond, while the diamond coating at the tip remained "inflexible." Any needed shaping of the diamond-coated regions for the purposes of implantation occurred prior to growth; the uncoated wire would provide the flexible electrical lead for the device. These electrodes are currently being analyzed for quality and stability. The extent of flexibility was explored with bending stress tests. MicroRaman spectroscopy, SEM, and electrochemical cyclic voltammetry were respectively assessing the sp^2 vs. sp^3 content, crystal size, and voltage window/baseline current of the diamond film.

350. Advanced Carbon Electrocatalyst Support Materials

Greg Swain, Doo Young Kim, Ayten Ay, Vermon M. Swope and Liang Guo, Department of Chemistry, Michigan State University, East Lansing, MI

High surface area carbon powder (sp^2-bonded) is used as an electrocatalyst support in proton exchange membrane (PEM) fuel cells. The carbon is a key component of the all-important membrane electrode assembly (MEA) where the oxygen reduction and hydrogen oxidation reactions occur, and electricity is produced. Structurally, the MEA is a complex material system comprised of a solid polymer membrane as an electrolyte and porous carbon black supporting Pt electrocatalyst as the anode and cathode (1). Improving the MEA stability is an important area of research these days because significant improvement in the durability is needed if PEM fuel cells are to find widespread application in transportation and stationary power. Microstructural degradation and corrosion of the carbon electrocatalyst support is a critical hurdle to cross in order to achieve the targeted fuel cell lifetimes. Carbon can undergo electrochemical oxidation during certain transient operations such as start-up/shut-down and local H_2 starvation. Advanced carbon materials are needed that undergo substantially less microstructural degradation and carbon corrosion at anodic potentials (ca. 1.2-1.4 V vs. RHE). High surface area, electrically conducting diamond powders function well as dimensionally stable supports. As an example, we compare the physical, chemical and electrochemical properties of glassy carbon powder before and after overcoating with a thin film of boron-doped ultrananocrystalline diamond. Evaluation of the corrosion resistance and dimensional stability were made in the presence of a Pt adlayer.

Inorganic Chemistry: Younger Inorganic Chemists

Sponsor: Division of Inorganic Chemistry
Organizer: John Protasiewicz Case Western Reserve University, Cleveland, OH
Presider: John Protasiewicz Case Western Reserve University, Cleveland, OH
Presider: Scott D. Bunge Kent State University, Kent, OH

Session Overview: This session showcases a number of invited younger and newer faculty speakers across the Ohio region.

351. Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes

Sumit Chakraborty, Graduate Student, J. A. Krause and **Hairong Guan, Professor**, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Nickel PCP-pincer hydride complexes catalyze the chemoselective hydrosilylation of C=O bonds of aldehydes and ketones in the presence of other functional groups. The mechanism involves C=O insertion into a nickel-hydrogen bond, followed by cleavage of the newly formed Ni-O bond with a silane.

352. Recent Highlights in Tetralkylguanidinate Coordination Chemistry

Scott D. Bunge, Department of Chemistry, Kent State University, Kent, OH

Designing a ligand for metal-organic complexes with discrete stoichiometric and catalytic reactivity has traditionally involved a delicate interplay between the steric and electronic components of the molecule and the coordinative saturation of the metal center. A general strategy to achieving an appropriate balance between these forces would be a conveniently obtained 'universal' ligand, capable of facilitating coordinative saturation while hindering entropicly driven disassociation. Our research group has developed a novel series of monoanionic 1,1,3,3-tetraalkylguanidinate (TAG) and neutral H-TAG ligands. The primary objective for developing this unique ligand set is to produce well-defined low-coordinate main group, transition metal and lanthanide compounds with enhanced and/or tailored reactivity. Our results have produced family of structurally characterized complexes representing each area of the Periodic Table. This presentation will present an overview of our results related to this area of coordination chemistry.

353. Arylthiolate Coordination Chemistry at Pseudotetrahedral Ni(II) Centers

Michael Jensen[1], Swarup Chattopadhyay[1], Tapash Deb[1], Huaibo Ma[1], Jeffrey L. Petersen[2] and Victor G. Young[3], (1)Department of Chemistry and Biochemistry, Ohio University, Athens, OH, (2)C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV, (3)Chemistry, University of Minnesota, Minneapolis, MN

Nickel-thiolate interactions are a ubiquitous feature in the active site ligand fields and turnover mechanisms of several environmentally significant bacterial metalloenzymes. We have prepared a number of high-spin Ni(II) complexes supported by tris(pyrazolyl)borate ligands with arylthiolate co-ligands (S. Chattopadhyay, et al. Inorg. Chem. **2008**, 47, 3384-3392). Ongoing structural and spectroscopic studies have revealed a surprising diversity of coordination modes for arylthiolate ligation in such complexes, which can be manipulated by steric modulation of the supporting scorpionate ligand. Such effects support in turn a mechanistically rich reactivity with electrophiles. Extension of this investigation to isoelectronic phenolate ligands will also be discussed.

354. Polymorphism In M(ethylenediamine)$_3$MoS$_4$ (M = Mn, Co, Ni)

Catherine M. Oertel, Hadley A. Iliff, Lee J. Moore and Hengfeng Tian, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH

Tetrathiomolybdate anions, MoS_4^{2-}, are precursors to hydrodesulfurization catalysts and can also be viewed as building blocks for functional hybrid inorganic-organic materials. Compared with the large number of network compounds based on group VI oxides, relatively few hybrid compounds have been prepared with tetrathiometallates as structural components, partly due to the challenges of crystallizing sulfide-based networks. A new polymorph of Ni(ethylenediamine)$_3$MoS$_4$ has been prepared solvothermally and characterized by powder and single crystal X-ray diffraction. Solvothermal reaction temperature is the most important parameter in controlling polymorph formation. The new polymorph is favored between ambient temperature and 80^{o}C, and a polymorph previously prepared by Bensch and coworkers is favored at higher temperatures. Water content in the reaction mixture and the anion (Br^- or NO_3^-) provided by the nickel(II) starting material also affect the phase composition of the product. Two new compounds, Co(ethylenediamine)$_3$MoS$_4$ and Mn(ethylenediamine)$_3$MoS$_4$, have been prepared and found to crystallize only in phases that are isostructural to the new polymorph of the nickel analogue. Thermogravimetric analysis and differential scanning calorimetry have been used to compare the stabilities of the compounds in the M(ethylenediamine)$_3$MoS$_4$ family, and detailed structural comparisons have been made.

355. Gilded Organometallics

Thomas Gray, Ph.D., David V. Partyka, James B. Updegraff, Miya A. Peay, Thomas J. Robilotto and Gao Lei, Chemistry, Case Western Reserve University, Cleveland, OH

Broad technological imperatives call for efficient luminescence from triplet-states: sensor design, light-emitting diode fabrication, *in vivo* photochemistry, and photodynamic therapy, among others. A proven entrée to triplet-state emitters is the heavy-atom effect, where emitting scaffolds incorporate high-Z elements. However, previous efforts have rarely ventured beyond iodine (Z = 53) in constructing phosphorescent organic species. The Gray research group (CWRU) undertakes new directions in gold (Z = 79) complex chemistry and the attendant photophysics. Existing organic fluorophores will be functionalized with (phosphine)- or (*N*-heterocyclic carbene)gold(I) fragments. These are isolobal with the proton and can bind to aromatic skeletons in place of terminal hydrogens. The gold(I) moiety is a relativistic functional group that endows organic ligands with spin-orbit coupling. Spin-selection rules thereby relax, and excited states of predominantly triplet character emerge. Fluorescent molecules become phosphorescent and photochemically active.

356. Catalytic Coupling Reactions Employing 3-Iminophosphine Palladium Catalysts

Joseph A. R. Schmidt, Department of Chemistry, The University of Toledo, Toledo, OH

Advanced organometallic catalysts for use in coupling reactions are not only essential for the improvement of multi-step syntheses of biologically important molecules, but can also provide highly atom-efficient green chemical methods for large-scale chemical production. High-yielding versatile syntheses have been established for the production of 3-iminophosphine ligands, allowing for the isolation of multi-gram quantities with high purity amenable to a wide range of backbone substitutions. The initial coordination chemistry of these ligands has been explored, resulting in the isolation and characterization of several target palladium complexes. In addition to traditional palladium-catalyzed coupling reactions, these complexes have been successfully utilized in the hydroamination of phenylacetylene and 1,3-cyclohexadiene. The catalytic activity and substrate preference observed using these 3IP-palladium catalysts is orthogonal to that observed in the previously reported late-metal systems, lending great value to these new catalysts as the ideal complement to existing technology. Initial investigations into the mechanism of this hydroamination reaction will be presented, in addition to stoichimetric reactivity relevant to the synthesis of potential reaction intermediates.

357. Exploring COMPLEX Oxides and Graphene for Dye-Sensitized Solar CELLS: Synthesis, Assembly and Photoelectrochemistry

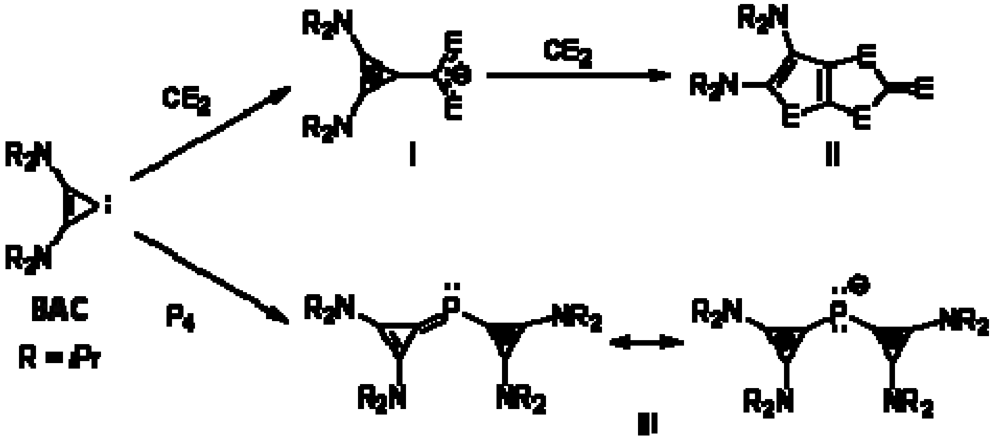
Yiying Wu, Department of Chemistry, Ohio State University, Columbus, OH

Dye-sensitized solar cells (DSC) is a promising alternative to the conventional Si p-n junction cells. An important component in DSC is the porous anode made of a wide-band-gap oxide for supporting sensitizers and conducting electrons. Previous efforts have been limited to binary oxides such as anatase TiO2, ZnO and SnO2 with little attention on complex oxides. However, complex oxides can provide the flexibility in tuning chemical and physical properties for dye anchoring and energy alignment. Complex oxides are also interesting for photocatalysis and transparent conducting electrodes. Therefore, a systematic study on complex oxides will have significant impact on photovoltaics and solar fuels. In this talk we will report Zn2SnO4-based DSC and discuss its advantages and limitation in comparison with TiO2, ZnO and SnO2. We have also developed photoelectrochemical methods to measure the band structure of Zn2SnO4. We have established the band gap and the positions of conduction band edge, ECB, and valence band edge, EvB. Such knowledge is essential for understanding the electron transfer at the oxide/electrolyte interface. Other oxides are under investigation, and promising preliminary results have been obtained. In addition, I will talk about the assembly and electrocatalytic performance of graphene. Graphene has been used as transparent conductor to replace FTO or ITO in DSC. We have investigated the fundamental electrocatalytic property of graphene films obtained from reduction of graphene oxide. In addition, we have also made an interesting discovery that graphene oxide nanosheets can be used for large-area, unidirectional alignment of nanowires.

358. Small Molecule Activation Via Stable Diaminocyclopropenylidenes: Formation of Electron Rich Heterocycles and Fragmentation of White Phosphorus

Glenn R. Kuchenbeiser, Bruno Donnadieu and Guy Bertrand, Department of Chemistry, UCR-CNRS Joint Research Laboratory (UMI 2957), Riverside, CA

Our recently isolated bis(diisopropylamino)cyclopropenylidene (BAC) undergoes nucleophilic activation of small molecule substrates such as carbon dioxide, carbon disulfide, carbodiimides, isocyanates, and white phosphorus. Due to the substantial reduction in $C_{carbene}$ bond angle of BAC (57°) relative to NHCs (ca 100°), as well as their increased ring strain, reactions of BAC with heterocumulenes leads first to betaines **I** which can then undergo a second addition and ring expansion to form electron rich bis-adduct heterocycles **II**. Reaction of BAC with P_4 leads to the first observed fragmentation of elemental phosphorus using neutral carbon reagents, affording ionic P_1, P_2, and P_3 fragments. The P_1 fragment **III** is isoelectronic to carbodicarbenes. These reactions are mild, operating at room temperature, and bypass the need for costly transition metal reagents.



Organic Chemistry: Nucleic Acids, Peptides, and Glycans (1)

Sponsor: ACS Division of Organic Chemistry, Quanta BioDesign, Ltd., Toledo Section of the ACS
Organizer: Xue-long Sun Cleveland State University, Cleveland, OH
Organizer: Steven J. Sucheck University of Toledo, Toledo, OH
Presider: Jun J. Hu University of Akron, Akron, OH
Presider: Xue-long Sun Cleveland State University, Cleveland, OH

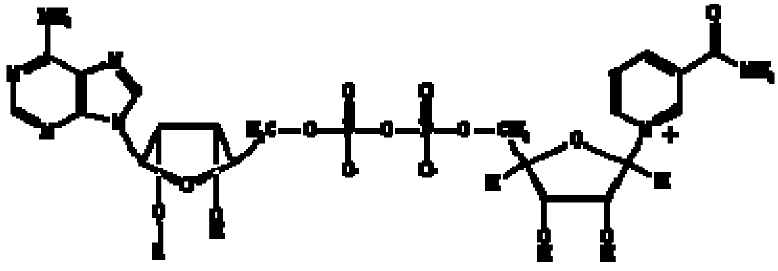
Session Overview: During the past decades, we have witnessed remarkable advances in bimolecular science in terms of new synthetic and discovery methodologies. This symposium aims to bring together chemists, biologists, and material scientists who use a variety of synthetic chemistry, chemical biology, bioanalytical chemistry as well as biomimetic research tools on nucleic acids, peptides, and glycan research. This symposium provides a platform to discuss and present the latest developments in the exciting area of chemistry of biomolecules and related compounds.

359. Non-Redox Metabolism of Pyridine Dinucleotides

James T. Slama, Ph.D., Department of Medicinal and Biological Chemistry, University of Toledo College of Pharmacy, Toledo, OH

NAD and NADP are crucially important co-enzymes with well established roles in energy production and in the biosynthesis of primary metabolites. Both of these pyridine dinucleotides also serve as

substrates in a wide variety of processes in which the pyridine-ribose bond is broken enzymatically, nicotinamide is released, and the ADP-ribose moiety of the dinucleotide is transferred to a nucleophilic acceptor. These non-redox reactions of NAD and NADP are important to cell regulation. In the nucleus, NAD can be polymerized to ADP-ribose polymers or consumed by Sir2 histone deacetylases. In a different context, NAD can be converted to cyclic ADP-ribose (cADPR) by the cell-surface enzyme CD38. Alternately, NADP and nicotinic acid react enzymatically to yield nicotinic acid adenine dinucleotide phosphate (NAADP). Both cADPR and NAADP are potent calcium-ion releasing 2nd messengers, and both are important in calcium-ion mediated intracellular signaling. We have synthesized novel pyridine dinucleotide analogs which we apply in the study of this intricate biochemistry. Our recent work focuses on the chemoenzymatic synthesis of derivatives of cADPR and of NAADP.



Nicotinamide Adenine Dinucleotide (NAD) R = H
Nicotinamide Adenine Dinucleotide phosphate (NADP) R = PO_3^{-2}

360. A Slippery Quadruplex Structure in the 5'-UTR of Human VEGF mRNA Is Essential for IRES Mediated Translation Initiation

Soumitra Basu, Mark Morris and Catherine Pazsint, Department of Chemistry, Kent State University, Kent, OH

It is well known that the RNA secondary and higher order structures formed in the 5'-untranslated region (5'-UTR) of cellular RNAs can block the ribosome scanning, thereby inhibiting the 5'-cap-dependent translation initiation process. Recent studies suggested that putative RNA quadruplexes located within the 5'-UTR can inhibit translations occurring via a 5'-cap-dependent mechanism. However, there are suggestions on the possible roles of RNA G-quadruplexes in 5'-UTR that they may aid in cap-independent initiation of translation. Herein, we show that an unprecedented ‘slippery’ G-quadruplex structure located within the internal ribosomal entry site A (IRES-A) of the 5'-UTR of human vascular endothelial growth factor (hVEGF) mRNA is essential for initiation of the cap-independent translation process. The formation of the quadruplex structure was indicated by circular dichroism (CD) spectroscopy, native gel electrophoresis, and enzymatic footprinting with RNase T1. Interestingly, the quadruplex forming region contains six tandem G-rich patches, two patches more than the minimum needed to form an intramolecular G quadruplex. Deletion analyses of the hVEGF IRES-A present in the context of a bicistronic dual luciferase reporter system show that the sequence provides redundancy to guarantee the formation of RNA structures that are critical for the cap-independent translation initiation. This is the first example of a functional slippery RNA quadruplex structure, which can be a novel mechanism to control translation initiation in a cap-independent manner.

361. Chemical Mechanisms of Nucleic Acid Damage

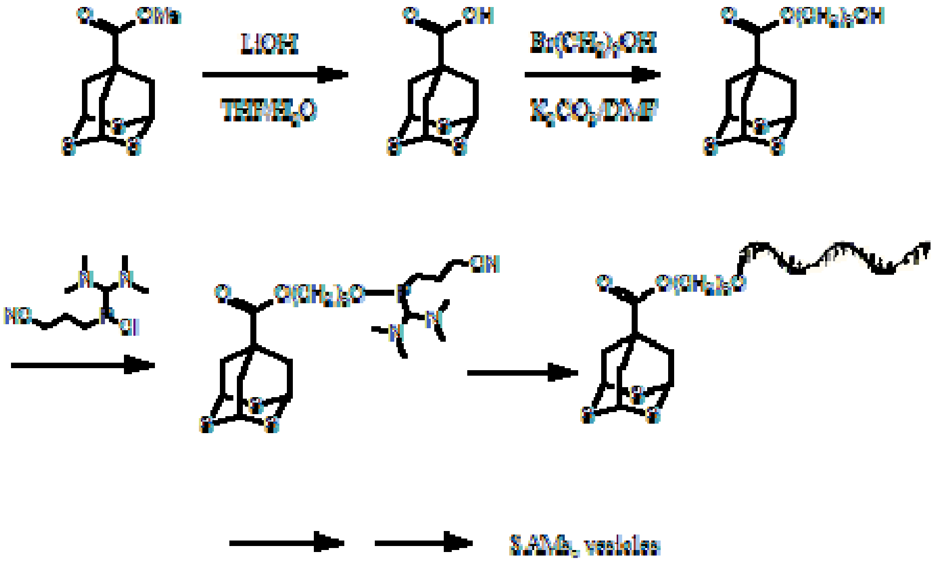
Amanda Bryant-Friedrich, Chemistry, University of Toledo, Toledo, OH

DNA oxidation at the 2-deoxyribose moiety has been implicated in the toxicological effects of oxidative stress. The small highly reactive products that result from sugar oxidation arise from initial damage events, complex DNA lesions, and the further degradation of unstable initially formed lesions. Their lingering presence in the cell ultimately leads to the modification of cellular constituents including DNA adduct formation and protein modification. The study of this process is greatly facilitated by the use of site-specifically modified nucleic acids that are capable of generating radicals that naturally form in DNA under conditions of oxidative stress. These radical precursors allow for the study of the products of oxidative damage and their decomposition in a controlled fashion. This controlled generation of oxidative damage also presents tools for use in the study of DNA damage repair.

362. 2,4,9-Trithiaadamantane Achored DNA and RAN On Au Film and Nanoparticle Surfaces

Jun J. Hu, Chemistry, University of Akron, Akron, OH

We report the synthesis and characterization of a stable and reliable surface linker for anchoring DNA and RNA to Au films and nanoparticles.



363. Engineering Improved Biosynthetic Antifreeze Protein Constructs through Bioconjugation and Oligomerization

Nolan B. Holland, Department of Chemical & Biomedical Engineering, Cleveland State University, Cleveland, OH

Standard molecular biology techniques have progressed to the point that the design and biosynthesis of protein-based materials is readily achievable. In addition to obtaining genes for proteins and polypeptides from organisms, they can be designed from scratch. Using recombinant methods, these genes for different protein domains can be combined to generate multifunctional proteins. For simple proteins with no post-translational modification, expression in bacterial systems is possible. The development of improved antifreeze proteins will be used as an example of this approach. Antifreeze proteins function by binding to ice crystal surfaces to inhibit their growth. Stabilizing ice crystals has promise in a wide range of applications including frozen food preservation, ice-slurries for refrigeration or air conditioning, and transplant organ or tissue storage. By increasing activity of these proteins, particularly at low concentrations, the amount of AFPs needed for a particular application will be reduced. In an attempt to mimic the high activity at low concentrations of a naturally occurring two-domain AFP, constructs with three or more domains have been designed either by adding an oligomerization domain to the protein or by bioconjugation of modified proteins to synthetic polymers. The novel protein constructs have been characterized by SDS-PAGE, size exclusion chromatography, circular dichroism, and, most importantly, thermal hysteresis measurements, which is used to compare the activities of these constructs to their single domain counterparts.

364. The Wonder of NO- Structure and Function Study of Nitric Oxide Synthase

Zhiqiang Wang, Chemistry, Kent State University, New Philadelphia, OH, Chin-chuan Wei, Department of Chemistry, Southern Illinois University, Edwardsville, IL and Dennis J. Stuehr, Pathobiology, Cleveland Clinic, Cleveland,, OH

Nitric oxide synthases (NOSs) are flavoheme enzymes that require cofactor tetrahydrobiopterin (H_4B) for activities (1). The influence of H_4B on NOS structure-function is complex. Single catalytic turnover studies suggest that H_4B plays a critical one electron donor to the heme-dioxy intermediate during catalysis. A few highly conserved amino residues uniquely interacted with H_4B via hydrogen bonding or aromatic stacking. We utilized point mutagenesis to investigate how these residues modulate H_4B function in different NOS isoforms. 5-methyl H_4B was also utilized in place of H_4B to study how the pterin ring structure influences redox behavior in NOS catalysis.

The unique catalytic profiles of NOS arise from differences in three kinetic parameters: Their rates of ferric heme reduction (kr), ferric heme-NO dissociation (kd), and ferrous heme-NO oxidation (kox) (2). Only a modest variation in kd exists among the three mammalian NOS isoforms. However, a bacterial NOS- `Bacillus subtilis NOS` exhibits a 10- to 20-fold slower kd rate compare to mammalian NOS counterparts. A conserved amino acid near the heme pocket was identified to be capable of affecting the NO release rate (3). To further investigate how this residue helps regulating the NADPH-driven NO synthesis, V346I mutant was generated and characterized. Optical spectra of the several heme species, NO synthesis activities, NADPH oxidation, heme reduction and heme-NO oxidation rate were measured and compared to the wild type enzyme. The results suggest that the slower kd along with the slower kox direct more enzyme into a none-productive pathway, thereby decreased mutant's NO synthesis activity.

365. Dissecting Large Cell Adhesion Complexes Using NMR Spectroscopy

Jun Qin, Cleveland Clinic, Cleveland, OH

Cell adhesion and migration are fundamental cellular responses, which are controlled by transmembrane receptor integrin and its dynamic associations with extracellular matrix (ECM) and intracellular actin cytoskeleton. The molecular events involving the ECM-integrin-actin linkage are highly complex. Here I will discuss how we utilize solution NMR spectroscopy as a unique technique to obtain atomic insight into this linkage. I will also present structural and functional data to elucidate how this linkage may be regulated to trigger cell adhesion and migration, and how it is dysregulated in human diseases. Agents may be developed from these studies to interfere with the dysfunctional processes for understanding the pathogenesis of the diseases and possibly for the disease treatment.

Physical Chemistry (2)

Organizer: Sarah J. Schmidtke College of Wooster, Wooster, OH
Organizer: Carlos E. Crespo-Hernández Case Western Reserve University, Cleveland, OH
Presider: Carlos E. Crespo-Hernández Case Western Reserve University, Cleveland, OH
Presider: Sarah J. Schmidtke College of Wooster, Wooster, OH

366. Photochemistry and Photophysics of DNA Structures From A-Tracts to Z-DNA

Bern Kohler, Department of Chemistry, The Ohio State University, Columbus, OH

The vulnerability of the genome to photodamage by solar UV light has sustained interest in excited electronic states in DNA for decades. Progress in understanding the nature and dynamics of electronic excitations in DNA has accelerated rapidly thanks in part to advances in quantum chemistry and ultrafast spectroscopy. Most excitations in single DNA bases decay nonradiatively in hundreds of femtoseconds. Surprisingly, much longer-lived excited states are observed in single- and double-stranded DNAs. Localized charge transfer states are prominent in runs of contiguous adenine bases (A tracts). These dark states are formed on a subpicosecond time scale from initially populated excitons. DNA is somewhat flexible and can adopt a range of structures beyond the iconic B-form double helix. The effect of helix conformation on excited-state dynamics has been studied in a double-stranded oligonucleotide that can be switched between B- and Z-forms. Experiments on G quadruplex structures and on `i`-motif DNA reveal that these forms have quite long-lived excited states compared to ones observed in duplex DNA. Structural changes to DNA profoundly affect the observed photoprocesses through alterations to base stacking and hydrogen bonding.

367. Attacking the Excited States of DNA with Some New Quantum Chemistry Tools

John Herbert, Department of Chemistry, The Ohio State University, Columbus, OH

Ab initio investigation of the excited electronic states in DNA multimers is quite challenging, due in part to the large model systems that are required in order to support delocalized exciton states. In principle, time-dependent density functional theory (TD-DFT) is affordable enough to be applied to systems comprised of many (> 10) base pairs, though in practice conventional TD-DFT calculations suffer from pathological underestimation of charge-transfer excitation energies, which often renders this method useless in large systems. We have addressed this deficiency using long-range-corrected density functionals that exhibit the correct asymptotic energy-versus-distance dependence for charge-transfer and other ionized states. While not a panacea, this methodology has allowed us to make progress in understanding the excited-state potential energy surfaces of DNA multimers, and in particular, the location of charge-transfer excited states relative to the excitonic bright states. This talk will describe both our new computational tools, as well as initial results regarding the excited states of DNA.

368. Solvent and Structural Effects On Charge Transfer in Para-Aminobenzoic Acid Derivatives

Sarah J. Schmidtke, Daniela Canache, Elana Stennett, Marnie Novak and Mary Kate Lockhart, Department of Chemistry, College of Wooster, Wooster, OH

Excited state charge transfer reactions are important chemical phenomena with biological applications to processes such as DNA mutagenesis and technologically for materials used as sources of tunable stimulated emission. The impact of molecular structure and solvent-solute interactions on the excited state reactions of a series of `para`-aminobenzoic acids (PABA) and corresponding ester derivatives is examined using a combination of experimental spectroscopy and quantum calculations. Following photoexcitation PABA derivatives may undergo an intramolecular charge transfer (ICT) resulting in the formation of a zwitterionic species. The presence and extent of the ICT can be traced through fluorescence spectroscopy, as both the neutral and charge-separated species are fluorescent. The molecular substituents and solvent environment influence the ICT. The present investigations work to quantify the thermodynamics of the process through the use of temperature-dependent fluorescence measurements. A range of solvents are used to examine the role specific solvent-solute interactions play upon the thermodynamics of the ICT. Initial time-resolved fluorescence measurements indicate differences in the timescales for emission from the locally excited and zwitterionic species, as well as solvent variations in the dynamics. Quantum calculations are used to provide a molecular level picture to complement bulk spectroscopic measurements. The fundamental studies provide a deeper understanding of the role that structure and solvent environment play upon the intramolecular charge transfer reactions.

369. Photophysical Properties of N-Confused Porphyrins

David A. Modarelli, Department of Chemistry and The Center for Laser and Optical Spectroscopy, The University of Akron, Akron, OH

N-Confused porphyrins (NCPs) are porphyrin analogs having one inverted pyrrole ring. The change in the structure of the porphyrin macrocycle leads to significant changes in the optical properties of the NCP compared to the analogous regular free base porphyrins. We have used a combination of steady state absorption and fluorescence spectroscopies as well as time-resolved fluorescence and transient absorption experiments to determine the photophysical properties of the two tautomeric forms (**1e** and **1i**) of 5,10,15,20-tetraphenyl N-confused porphyrins. We have also used time-dependent density functional (TD-DFT) calculations to determine the ground state (S_0) geometries and gas-phase and solvation-based ground state absorption spectra of **1e** and **1i**, as well as the unsubstituted parent NCPs **2e** and **2i**. TD-DFT calculations were also used to predict the Franck-Condon and relaxed S_1 and S_2 excited state geometries for **2e** and **2i**. The absorption spectra of the oxidized and reduced forms of **1e** and **1i** have also been determined, and the structures of these radical ions computed. The incorporation of N-confused porphyrins into arrays for energy and electron transfer will be discussed in the context of these results.

370. Exploring the Photophysics of Conjugated Pt^{II} Acetylides

Aaron A. Rachford, Sébastien Goeb and Felix N. Castellano, Department of Chemistry & Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH

For nearly a decade and a half, fundamental and applied research has continued to expand and exploit the photochemistry and photophysics of platinum(II) polyimine acetylide complexes for a variety of applications such as optical power limiting, electroluminescence, singlet oxygen sensitization, cation sensing, and vapochromism. This large body of applications is a result of the rich photochemistry and photophysics presented by this molecular motif. Through systematic variations in the physical and electronic structure of the charge-transfer and ancillary acetylide ligands along with appropriate model complexes, we are able to observe dramatic shifts in the excited-state energies of various complexes. Some consequences of the structural modifications within this family of chromophores include long-lived room temperature emission with solvent programmable photoluminescence, picosecond intramolecular sensitization of intra-ligand excited states, as well as near-IR emission and sensitization of ${}^1O_2$ phosphorescence. Steady-state and time-resolved absorption and emission spectroscopy are employed to elucidate the nature of the excited-states exhibited by these complexes. The effect of designing molecules with energetically proximate triplet excited states will be presented and discussed.

371. Effects of Aggregation On the Electronic Properties of Polythiophene and Its Oligomers

Kelly L. Zewe, Linda Peteanu and Wynee Lee, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA

Polythiophene is a commonly used component of organic electronics and solar cells. Polythiophene chains are readily aggregated under the processing conditions used to form thin films for applications in devices. This aggregation can drastically alter the charge transfer and optical properties of the material. In order to better understand these effects, oligomers of polythiophene were studied. Because oligomers have shorter, well-defined chain lengths and are free of defects, the effects of aggregation on their electronic properties are easier to interpret than those of the polymer systems and are more readily modeled using electronic structure theory. Bulk and single-molecule fluorescence methods are used to explore the emission properties as a function of aggregate size, precipitating solvent, and monomer properties and to correlate these to the polymer properties.

372. Electronic-to-Vibrational Energy Transfer From $Cl^*(^2P_{1/2})$ to $CH_4(v_4)$ and $CD_4(v_4)$

David A. Dolson and Brian R. Munson, Department of Chemistry, Wright State University, Dayton, OH

Electronic-to-vibrational (E-V) energy transfer is a significant kinetic channel in the collisional quenching of spin-orbit excited chlorine atoms, $Cl^*(^2P_{1/2}, 882\ cm^{-1})$, by molecular collision partners. In the present study Cl* atoms are prepared in the presence of CH_4 or CD_4, under pseudo first-order conditions, by photolysis of ICl at 532 nm with a pulsed Nd:YAG laser. Quenching of Cl* by CH_4 or CD_4 results in E-V excitation of the v_4 asymmetric bending mode as observed by infrared (IR) fluorescence from the vibrationally excited products. Time-resolved IR fluorescence observations of $CH_4(v_4)$ and $CD_4(v_4)$ are consistent with a simple kinetic scheme involving direct E-V excitation of $CH_4(v_4)$ or $CD_4(v_4)$ followed by a slower collisional relaxation. The total quenching rate of Cl* is reflected in the rise of the v_4 fluorescence signal. The total Cl^* bimolecular quenching rate coefficients (± 2σ) obtained in this study at 298 ± 2 K are $(1.9 \pm 0.5) \times 10^{-11}\ cm^3 \times molecule^{-1} \times s^{-1}$ for quenching by CH_4 and $(1.4 \pm 0.9) \times 10^{-10}\ cm^3 \times molecule^{-1} \times s^{-1}$ for CD_4. Intensity measurements interpreted within this kinetic scheme indicate that the E-V channel for v_4 mode excitation accounts for ≈30% of the total quenching of Cl^* by CH_4 and CD_4. It is remarkable that the E-V branching ratios are the same in both systems even though the v_4 – Cl* energy differences span a four-fold range from approximately ½kT (CD_4) to 2kT (CH_4).

SAS/AVS Applied Spectroscopy Symposium (2)

Sponsor: De Nora Tech ThermoFisher Scientific Bruker BioSpin Corporation Shimadzu Scientific Instruments, Inc.
Organizer: Wayne Jennings, Ph.D. Case Western Reserve University, Cleveland, OH
Organizer: Brian Perry, Ph.D. LORD Corporation, Erie, PA
Presider: Mike Setter, Ph.D. John Carroll University, University Heights, OH

Session Overview: The SAS/AVS symposium will feature papers on the utilization of spectroscopy for academic and industrial applications. The SAS/ACS Yeager Award talk for outstanding undergraduate research involving spectroscopy will also be featured in the symposium.

373. Boundary Film Composition and Formation From Synergistic Combinations of Surface Active Compounds

Douglas T. Jayne, The Lubrizol Corporation, Wickliffe, OH

In recent years, much progress has been made toward inventing new compounds for antiwear (AW) that are free of metals (ash) and other heteroatoms such as phosphorus and sulfur. A class of compounds was found that consisted entirely of nitrogen, oxygen, carbon and hydrogen (NOCH) that was especially efficacious in these regards. Innovation and improvements in wear and friction opens the door to product differentiation in future engine oil specification upgrades.

A broad scope of NOCH antiwear molecules was synthesized and tested and a wealth of practical and fundamental knowledge was obtained. While this work helped build a rudimentary structure-performance understanding, very little was known about the specific chemical mechanism by which these components acted at surfaces and with other components. A better understanding of mechanism could lead to building a more perfect anti-wear molecule. Additionally, an understanding of how these molecules interact with other components can help us strengthen the performance of these AW additives even further.

In this work, the action of various organic derivatives when combined with other single components, binary components, and fully formulated fluids was investigated. Oils were subjected to reciprocating wear tests under pure sliding conditions using steel parts. The surfaces of the parts at the end of test were analyzed with scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). These organic derivatives interact with other components such as detergents and zinc dithiophosphates to modify steel surfaces in intriguing ways. Surface composition and the current understanding of the mechanism of film formation will be discussed.

374. Direct Probe CI-MS and APCI-MS for Direct Materials Analysis

Robert P. Lattimer and Michael J. Polce, Lubrizol Advanced Materials, Cleveland, OH

Over the past several years our laboratory has emphasized methods for direct polymeric materials analysis. In this regard, direct probe chemical ionization (isobutane DP-CI-MS) has been a mainstay in the detection and identification of residual chemicals, additives, and polymer components (via pyrolysis) in formulated materials. Within the past year we have added Pyroprobe^R atmospheric pressure chemical ionization (Py-APCI-MS) to our laboratory as a supplement to DP-CI-MS. For DP-CI-MS, the material (~1-2 mg) is heated `in vacuo` (~30-450^{o}C) in the direct probe of a quadrupole mass spectrometer, with analysis by isobutane CI-MS. For Py-APCI-MS, the material is heated in air (~30-1000^{o}C) in the coil probe of a "pyrolysis probe" (CDS Pyroprobe 5000), with analysis by APCI-MS. With either method, residual chemicals and more volatile additives are detected early in the heating process (up to ~200-300^{o}C), while polymer pyrolysis products are detected later in the run (above ~250-300^{o}C, depending on the polymer). Quadrupole DP-CI-MS is a low resolution technique, but Py-APCI-MS as practiced in our laboratory adds APCI-MS/MS and high resolution capability.

DP-CI-MS and Py-APCI-MS are complementary techniques; they provide similar, but not the same, data. Our experience shows that DP-CI-MS gives a more stable ion current, less background, less fragmentation, and more predictable and reproducible spectra. Py-APCI-MS, on the other hand, provides a higher maximum temperature and a means by which to carry out sample heating at atmospheric pressure (to mimic thermogravimetric analysis, TGA). Py-APCI-MS allows one to carry out direct probe analysis using modern APCI/ESI instruments with MS/MS and high resolution capability.

375. From Wavenumbers to Batch Numbers: Using Vibrational Spectroscopy to Support Pharmaceutical Manufacturing

John P. Bobiak, Gary McGeorge, Dimuthu Jayawickarama, Boyong Wan and Dongsheng Bu, Analytical Research and Development, Bristol Myers Squibb Co., New Brunswick, NJ

Near-infrared (NIR) spectroscopy has played a key role in the evolution of pharmaceutical process monitoring for the manufacture of drug products. Since NIR spectroscopy is sensitive to chemical and physical attributes of the sample, careful attention needs to be paid to the many variables that impact the spectral response.

This presentation will describe: 1) efforts to understand and model these variations to produce robust analytical methods; and 2) applications of NIR techniques (bench, online, and imaging) to understand relationships between processing parameters and pharmaceutical product quality.

376. Multidimensional NMR Studies of Models for Krytox® Fluoropolymers

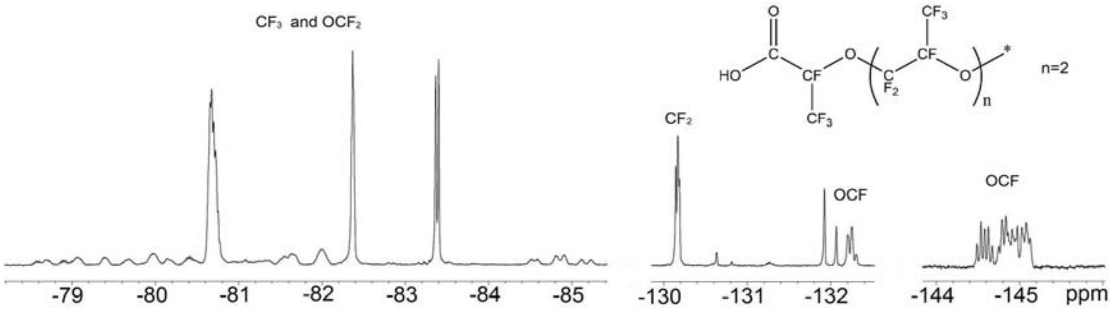
Xiaohong Li[1], Peter L. Rinaldi[1], Elizabeth F. McCord[2], Silapong Baiagern[1], Peter A. Fox[3], Sangrama Sahoo[4] and Silapong Baiagern[1], (1)Department of Chemistry, University of Akron, Akron, OH, (2)E. I. duPont de Nemours and Company, Wilmington, DE, (3)Dupont Performance Elastomers, Wilmington, DE, (4)Ashland Incorporated, Ashland Hercules Research Center, Wilmington, OH

Krytox®-fluoropolymers (KF) are well known for their superior lubricant characteristics when applied in computer disk devices and aerospace applications. It is of great interest to know their structural characteristics such as: monomer and stereo-sequence effects, chain end structures, and structure

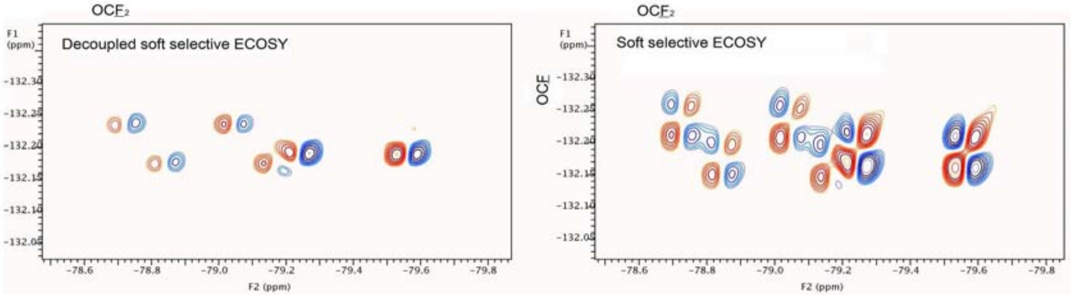
defects, which give valuable information about the chemistry of the polymerization process and physical properties.

Fortunately ^{19}F NMR is extremely useful for structure characterization, because of its large spectral window, its sensitivity to small structure variation, and long-range couplings (usually observable up to 4-5 bonds) which produce useful information within the spectra. In long chain molecules, however, these coupling interactions are often very complex, making it difficult to interpret ^{19}F NMR spectra. A method of sorting these interactions is needed to improve the speed and accuracy of structural interpretations. Selective excitation and selective decoupling modifications of ^{19}F-^{19}F COSY 2D-NMR experiment is the way to approach this problem. (1)

Model compounds K_4 and K_5, which are KF tetramer and pentamers, respectively, were used to test the utility of these experiments. The 1D - ^{19}F NMR of K_4 below shows three regions of resonances vary by structure.



Rather than collecting higher resolution COSY spectrum of entire spectral window (which would require an enormous amount of instrument time), various permutations of selective COSY spectra could be obtained to produce high resolution 2D spectra in a short time. Selective inversion pulses were incorporated to remove J_{FF} couplings and further simplify the spectra. Spectra with clear ^{19}F-^{19}F coupling interactions, like the one shown below, are obtained.



377. High Throughput Environmental Analysis by ICP-OES and ICP-MS

Fergus Keenan, Trace Element Analysis, Thermo Fisher Scientific, Mansfield, MA and Dan Wiederin, Elemental Scientific Inc, Omaha, NE

- The limitatons in environmental trace element analysis are matrix tolerance, interference removal, detection limits and sample throughput.
- Major technological advances in ICP-OES technology have produced instruments with vastly improved sensitivity and increased wavelength range that allow for reduced integration times and increased linear range resulting in superior performance in environmental analysis.
- The development of matrix tolerant interfaces in ICP-MS have removed a major barrier to high throughput analysis of soil, sediment and solid waste samples. In addition, 3rd

generation Collision Reaction Cell technologies allow for cost effective interference free analysis for the first time, even in the most challenging of matrices.

- Concurrent development of new high throughput sample introduction accessories has effectively doubled sample throughput without compromising instrument performance.

The technology behind these enhancements shall be discussed in detail and illustrated with real world data from current state of the art ICP-OES and ICP-MS instrumentation.

378. Certification and Validation of Simple or Complex Samples Via NMR

Joshua M. Hicks, Christian Fisher and Kimberely Colson, Bruker-BioSpin, Billerica, MA

Quality control of chemical reaction precursor materials and/or multi-component products are monitored by techniques established to confirm a samples purity, quality and, if possible, identification of adulterants. By defining and identifying properties of a substance early, considerable time and resources are not wasted, for example, in manufacturing errors. In addition, labeling restrictions and government regulatory guidelines, such as those in food safety and quality, are requiring an increasing amount of certification and validation of sample source and components. In order for a screening method to be successful the technique must be reproducible, timely, minimize handling loses, and provide accurate results to properly categorize the sample. NMR is unique as a non-destructive screening tool in that a single spectrum contains all of the data necessary to identify constituents and their quantities. Quality control of precursor materials by NMR is useful to identify and confirm the purity of the material, identify the contaminants, quantify the contaminants, and possibly identify other contaminants not listed. More complex analysis of NMR spectra using multivariate monitoring of constituents is used to distinguish mixtures based on properties such as quality, purity, and origin(s). Here the details and implementation of NMR as a screening tool are covered. From simple or complex mixtures, it is possible to reproducibly determine (1) compound identity, (2) identify the individual components and/or adulterants in a mixture, (3) accurately and quantitatively measure those constituents, and (4) discriminate mixture origin using multivariate techniques.

379. Methods for Enhancing Chemical Contrast for Hyperspectral Data

Nikolas J. Neric, B.S., Anita Wiederholt and John F. Turner II, Department of Chemistry, Cleveland State University, Brooklyn, OH

The reduction of hyperspectral image data sets into a single image frame that exhibits chemically relevant image contrast is the chief aim of chemical imaging. While there are many powerful chemometric methods such as factor analysis and principle components analysis that are widely used to perform hyperspectral image processing, these methods are assisted methods and can result in erroneous analyses if they are applied to new chemical systems without adequate training data. Our work focuses on the development of a completely automated method for generating enhanced chemical image contrast that relies on no a priori chemical information. Our immediate aim is to develop a strategy for choosing a reference vector for spectral identity mapping (SIM) that minimizes angular symmetry in the chemical image while preserving as much of the original data variation as possible. We discuss the advantages and shortcomings of conventional approaches for selecting reference vectors and provide a theoretical framework for selecting more effective spectral vectors. In addition, we compare methods for generating multispectral image contrast with the novel algorithm presented here.

380. ATR Imaging for Analysis of Complex Materials

Louis G. Tisinger, Ph.D., PerkinElmer, Oak Brook, IL

The ability to resolve layers using FTIR microscopy is often challenging, due to the very thin nature of layers in laminates. Tie layers, for example, can be less than 5 micrometers thick, which can be difficult to resolve in a typical FTIR single-point transmission analysis, where an aperture is used to define sample area. Apertures reduce spatial resolution as they are closed to smaller dimensions. In contrast, array detectors improve spatial resolution, owing to the absence of an area-defining aperture; the detector elements define the sample area interrogated. However, full-width-half-maximum spatial resolution is theoretically limited to about one wavelength for a typical system. Spatial resolution can be improved significantly by using ATR with an FTIR imaging microscope. This presentation will show examples of ATR imaging analyses conducted on polymer laminates and a biomedical sample.

Small Chemical Business: Entrepreneurship and Innovation Workshop

Sponsor: The Kauffman Foundation and the ACS Division of Small Chemical Business.
Organizer: Joseph E. Sabol CHEMICAL CONSULTANTS, Racine, WI
Presider: Joseph E. Sabol CHEMICAL CONSULTANTS, Racine, WI

Session Overview: Thinking about starting a business? Is entrepreneurship right for you? Already have a business? Is your strategy in place to grow? Representatives of the Kauffman Foundation, the largest foundation dedicated to advancing entrepreneurship in America, will facilitate a workshop with relevant, practical "just-in-time" information, tools, and resources - all designed to assist aspiring and existing entrepreneurs who are building companies that innovate and create jobs and wealth. This session will include interactive exercises and facilitated discussions around starting and running high-impact companies. If you have a business idea or already lead a business, bring your thirty-second elevator pitch to share.

381. Tools for Entrepreneurs

Todd Smith, Manager, Entrepreneur Learning Programs, Ewing Marion Kauffman Foundation, Kansas City, MO

Thinking about starting a business? Already have a business? A representative of the Kauffman Foundation, the largest foundation dedicated to advancing entrepreneurship in America, will share a variety of relevant, practical "just-in-time" information, tools, and resources to assist aspiring and existing entrepreneurs who are building companies that innovate and create jobs and wealth. This session will include interactive exercises and facilitated discussions around starting and running high-impact companies. If you have a business idea or already lead a business, bring your thirty-second elevator pitch to share.

Women in Electrochemistry (3)

Organizer: Carol Korzeniewski Texas Tech University, Lubbock, TX
Organizer: Heidi B. Martin Case Western Reserve University, Cleveland, OH
Organizer: Irina Serebrennikova Energizer, Westlake, OH
Presider: Irina Serebrennikova Energizer, Westlake, OH
Presider: Heidi B. Martin Case Western Reserve University, Cleveland, OH
Presider: Carol Korzeniewski Texas Tech University, Lubbock, TX

382. Recent Materials Advances in PEM Electrolysis

Katherine E. Ayers, Director of Research, Proton Energy Systems, Wallingford, CT

Hydrogen generation from renewable energy sources during peak production times for use during low production periods is one attractive solution to the energy crisis. Advantages of this approach include hydrogen’s high gravimetric energy density and the ability to separate generation from storage in contrast to battery technology. Water electrolysis has benefits over other hydrogen generation technologies due to the lack of carbon footprint when integrated with a renewable source of energy. Specifically, proton exchange membrane (PEM) electrolysis is a promising technology for hydrogen generation applications such as fueling and backup power because of the lack of corrosive electrolytes, small footprint, and ability to generate at high pressure, requiring only deionized water and an energy source. PEM electrolysis also produces very pure hydrogen, with none of the typical catalyst poisons that may be found in hydrogen produced from reforming.

Proton Energy Systems has developed commercial PEM electrolyzers with outputs up to 12 kg/day of hydrogen. To date, over 1200 units manufactured by Proton have been installed worldwide, and the current stack design has demonstrated safe and reliable performance over tens of thousands of hours of operation. Recent development activity at Proton has led to an almost 20% improvement in efficiency in stack performance, while cost reduction efforts for the cell stack membrane-electrode-assembly (MEA) have netted nearly a 30% savings in material cost. This is significant considering that the MEA represents the single highest cost component within the electrochemical stack. This talk will focus on recent materials advances leading to these achievements.

383. Electrochemical and Spectroscopic Studies of Small Organic Molecule Oxidation On Low Index Platinum Electrodes

Rachel L. Behrens and Andrzej Wieckowski, Department of Chemistry, University of Illinois, Urbana, IL

As the interest in fuel cells grows, the search for a viable, high energy, direct oxidation fuel source continues to be essential for future progress and development towards widespread commercial availability. Fuels such as methanol, ethanol, and formic acid have been the forerunners for fuel cells while formic acid has been shown to be a viable fuel source for micro fuel cells. To study the poisoning effects of oxidation intermediates, we have examined the behavior of formic acid, ethanol, and acetic acid (as an undesired product of ethanol oxidation) undergoing oxidation on low index single crystal platinum electrodes, as well as polycrystalline platinum. Reaction intermediates are electrochemically deposited on the electrode surface during a chronoamperometric step, and the current is monitored while the electrode potential is scanned to desorb the intermediates. To more fully understand the mechanistic aspects of surface reactions, such as these oxidation reactions, the use of spectroscopic methods is required. For such spectroscopic studies, the intermediates at the electrode surface may be monitored in real time while the reaction progresses with broad-band sum frequency generation (BB-SFG). BB-SFG is surface-sensitive, as the signal is generated only at the surface-liquid interface where the centrosymmetry is broken. When combined with the electrochemical methodologies, the vibrational transitions of adsorbates at the electrode surface from the oxidation reaction may be monitored as a function of both electrochemical potential and time. With these data, we are able to compare the pathways of these reactions and oxidation potentials across the studied Pt catalyst surfaces.

384. Reaction Kinetics of Size and Shape Controlled Platinum Catalysts for a Homogeneous Catalytic Reaction with Methyl Viologen

Corinne A. Atkinson, Keith J. Stevenson and Allen J. Bard, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX

Correlating the structure and reaction kinetic properties of nanoparticle (NP) catalysts as functions of size and shape is a major challenge in analytical chemistry. Yet obtaining information of this kind would facilitate the discovery, characterization, and mechanistic understanding of new catalysts. We have designed a spectroelectrochemical method that uses methyl viologen (MV) as a redox-mediator to measure reaction kinetics at the surface of Pt nanoparticles (NPs) of various geometries dispersed homogeneously in solution. MV is stable in acidic, aqueous solution in both its dication (MV^{2+}) and radical cation ($MV^{+\bullet}$) forms. In the presence of Pt, however, $MV^{+\bullet}$ will reduce H^+ to molecular

hydrogen, H_2. In this presentation, we describe voltammetric experiments which use a carbon disk electrode to detect the formation of MV^{2+} when Pt NPs are dispersed in acidic buffer solutions. Scan rate dependent voltammetric studies enable us to estimate the degree to which the MV^{2+} forms, allowing us to extract kinetic information (rate constants) about the catalytic activities of size and shape dependent Pt NPs. The catalytic activity of the Pt NPs are also evaluated using UV-vis spectroscopy by monitoring the disappearance of $MV^{+\bullet}$ at 395nm. Using both approaches, we can elucidate to what degree NP size and shape influence the catalytic activity of Pt NPs.

385. Mitochondrial Bioelectrocatalysis

Shelley Minteer, Kevin Boehm, Marguerite Germain and Robert Arechederra, Chemistry, Saint Louis University, St. Louis, MO

Mitochondria are unique organelles in which they contain multiple metabolic pathways and contain all the enzymes necessary to completely oxidize pyruvate and fatty acids. They are generally considered the "powerhouse" of the living cell. We have investigated strategies for mediated and direct bioelectrocatalysis of mitochondria at carbon electrodes. These mitochondria modified electrodes have been used for oxidation of pyruvate and fatty acids in organelle-based biofuel cells and for self-powered explosive sensing due to the unique ability to actuate power in the presence and absence of nitroaromatic explosives.

386. Determination of the Electronic Density of States at the Fermi Level of Nitrogen Doped Carbon Nanotubes Using Electrochemical Impedance Spectroscopy

Jaclyn D. Wiggins-Camacho and Keith J. Stevenson, Department of Chemistry & Biochemistry, The University of Texas at Austin, Austin, TX

Heteroatom doping of graphitic carbon lattices affects various physicochemical properties of sp^2 carbon materials. In particular, nitrogen-doped nanocarbons have received attention as catalyst supports and electrochemical sensors. We are evaluating the advantages of the apparent intrinsic catalytic properties of nitrogen-doped carbon nanotubes (N-CNTs) when used as electrodes in electrochemical experiments. In this presentation, we discuss the influence of nitrogen doping of CNTs on their electrochemical and electrical properties such as the density of states at the Fermi level ($D(E_F)$), bulk conductivity and work function. Studies were performed on free-standing N-CNT electrode mats to understand the inherent electrochemical properties of the material without relying on another conductive support. N-doping levels ranging from 0 to 7.7 at.% N, were examined and electrochemical impedance spectroscopy (EIS) was used to evaluate the differential capacitance and to estimate the effective $D(E_F)$. A trend of increasing $D(E_F)$ with N-doping and the number of edge plane sites is observed. UV photoelectron spectroscopy (UPS) was used to probe the valence band of N-CNTs in order to estimate the work function of the mats. The work function linearly increased from 4.1 to 4.5 eV for increasing N-doping levels. The bulk electrical conductivity of the N-CNT electrode mats appears to be junction dominated as shown by the relationship between the bulk conductivity and average N-CNT length within the mats determined using high resolution scanning transmission electron microscopy (STEM). These findings indicate that N-CNTs should be considered as metallic electrodes with a finite density of electronic states at the Fermi level.

387. H2 Reactivity of Pd Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications

Monica Moreno and Francis P. Zamborini, Department of Chemistry, University of Louisville, Louisville, KY

Our group recently demonstrated the use of metal nanoparticles (Pd, Pd/Ag and Pd/Au) protected with different organic groups for electronically sensing H_2 at low concentrations. Alkyl thiol-coated Pd nanoparticles are not reactive to H_2, requiring high temperature, treatment and conditioning in pure

H_2 gas to obtain an operational device. Alkyl amine-coated Pd, Pd/Ag or Pd/Au nanoparticles react with H_2 without ozone or high temperature treatment, but undergo large irreversible changes in morphology and loss of organic material. In order to improve the reactivity to H_2 while minimizing the number of pretreatment steps and preventing large morphology changes, we evaluated Pd nanoparticles containing different ratios of hexanethiol and octylamine ligand on their surface, synthesized by liquid-phase place-exchange. At optimized ratios these films respond reversibly to H_2 down to 0.50% without significant conditioning, multiple treatments or irreversible morphology changes as determined by electronic measurements and verified by spectroscopy measurements of Pd nanoparticles in solution. The use of Pd nanoparticles with mixed monolayers offers H_2 reactivity, while maintaining structural stability necessary for sensing or catalysis applications.

388. Transmission Infrared Spectroscopy as a Probe of Structure and Hydration Effects in Fuel Cell Membrane Materials

Carol Korzeniewski and Chang Kyu Byun, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX

Infrared spectroscopy is being applied to investigate structural changes that occur in fuel cell membrane materials during hydration and dehydration. Transmission measurements are performed on cast films of sub-micron thickness and on freestanding membrane of approximately 50 micrometer thickness (i.e., Nafion 112). Upon exposure to humidified atmosphere, vibrational bands for water present within membrane pores and channels are detected. This presentation will discuss studies of water uptake by Nafion and vibrational spectral characteristics of Nafion in comparison to a new type of membrane material based on bis[(perfluoroalkyl)sulfonyl] imide ionomers (PFSIs). Least squares modeling techniques are being applied to infrared spectral data sets to distinguish differences in the properties of interfacial and bulk-like water in Nafion and to probe effects of water uptake on polymer structure. Water uptake detected by infrared absorbance measurements starting from membrane in a dry state follows a pore-diffusion model. Results of least squares modeling using the pore-diffusion equation reveal differences in the responses of hydrophobic and hydrophilic groups in Nafion during hydration. In studies of PFSIs, which differ structurally from Nafion mainly in the nature of the side chain end group, vibrational bands reveal differences in the electrostatic environment surrounding the side chains consistent with the relative sizes and structures of the end groups (sulfonate in Nafion and sulfonyl imide in PFSIs).

Undergraduate Student Research Poster Session

Organizer: Mark J. Waner John Carroll University, University Heights, OH
Organizer: Michael A. Nichols John Carroll University, University Heights, OH

Session Overview: Poster presentations highlighting undergraduate research contributions across the various subdisciplines of chemistry. Funding for the undergraduate program comes from the Undergraduate Programs Office of the ACS.

389. A Chemical Profile of Olentangy River

Ashley Bartman, Alex Cherry, Laura Sanman, Andrew Merriman and Ted M. Clark, Department of Chemistry, The Ohio State University, Columbus, OH

An extensive, student-led, characterization of the Olentangy River's water quality has been undertaken as part of the Research Experiences to Enhance Learning (REEL) program. Water samples were collected at sites along the Olentangy River in Columbus, OH, during the Fall of 2008. Chemical testing of these samples, accomplished within a quantitative analysis chemistry course at the Ohio State University, led to the determination of chloride, fluoride, phosphate, nitrate, nitrite, and trace metal concentrations. Additional tests examined water conductivity, bacteria levels, temperature, pH, water flow, and dissolved oxygen concentration. Results from these tests will be discussed in relation to characteristics of the river, e.g. the proximity of combined sewage overflows (CSOs), at selected testing sites.

390. Synthesis and Characterization of the Novel Perovskite Series $NaCo_xNi_{1-X}F_3$

Chad J. Miller and Tim R. Wagner, Department of Chemistry, Youngstown State University, Youngstown, OH

Novel perovskite-related compositions in the series $NaCo_xNi_{1-x}F_3$, for x = 0.1, 0.2…0.9, were synthesized and characterized along with their known ternary end-members by students in an undergraduate general chemistry laboratory course as part of the Project REEL implementation at Youngstown State University during spring, 2009. This previously unreported series ranges from dark pink to yellow-green in color and all compositions were found to have an orthorhombic lattice. The structure, composition, and optical properties were characterized via X-ray powder diffraction, X-ray fluorescence, and UV-Vis spectroscopy, respectively. Results of these experiments will be compared to those obtained previously from the $KCo_xNi_{1-x}F_3$ series of compositions.

391. Bioremediation of Selenium Containing Wastewater

Mike Booth, Department of Chemistry, West Virginia University Institute of Technology, Montgomery, WV

Soluble selenium compounds are an essential nutrient in many organisms. However greater than dietary concentrations of selenium is toxic and bioaccumulates in aquatic organisms through the food chain. High amounts of selenium results from agricultural activity, coal drainage wastewater, fuel refining, or any activity that disrupts the soil. Soluble selenium, such as selenate (SeO_4^{2-}), and selenite (SeO_3^{2-}), needs to be reduced to Environmental Protection's acceptable level of 5 ppb before it is disposed into aquatic systems. In recent years, several reports have described the bacterial reduction of selenium compounds to the less soluble and less toxic form, elemental selenium. The bacterial reduction process opens up possible scenarios for the exploitation of various bacterial strains in bioremediation protocols for the treatment of selenium bearing wastewaters. The goal of this project was to select and isolate selenium reducing bacteria, native to West Virginia.

Water samples were collected from coal impoundment ponds, and the bacteria present were grown in environments containing high concentrations of selenate and selenite. The bacteria survived by reducing the soluble selenium into less soluble, and less toxic, elemental selenium. Using the atomic absorption spectrophotometer the soluble selenium was monitored over a period of 48 days.

The concentration of the soluble selenium was greatly reduced, and with further development this bioremediation process could be used in bioreactors. In a bioreactor the elemental selenium would drop to the bottom and be collected. These bioreactors could be set up at waste water facilities to help them reach the EPA's regulations.

392. Synthesis and Characterization of the Novel Perovskite Series $NaCo_xFe_{1-X}F_3$

Ashley M. Wolf and Tim R. Wagner, Department of Chemistry, Youngstown State University, Youngstown, OH

Novel perovskite-related compounds in the series $NaCo_xFe_{1-x}F_3$, where x = 0.1, 0.2…0.9, were synthesized and characterized along with their ternary end-members by students in an undergraduate general chemistry laboratory as part of the Project REEL implementation at Youngstown State University during spring, 2009. This series has not been previously reported, and its colors range from dark pink to a light yellow with all compositions found to have an orthorhombic lattice. The structure, composition, and optical properties were characterized hands-on by the students via X-ray powder diffraction, X-ray fluorescence, and UV-Vis spectroscopy, respectively, and this data will be presented.

393. Controlling Particle Size and Morphology of Nanosized Cubic Zirconium Tungstate

Hassan Issa Baiz, Akena Latigo, Nathan Banek and Cora Lind, Department of Chemistry, The University of Toledo, Toledo, OH

Negative thermal expansion (NTE) materials contract when heated. A well-known example of a material exhibiting this phenomenon is cubic zirconium tungstate (ZrW_2O_8). This material displays strong negative thermal expansion from 0.3 to 1050 K. By mixing ZrW_2O_8 with a material that exhibits positive thermal expansion in a composite, the overall thermal expansion of the composite can be controlled. However, in order for this material to be suitable for use in composites, particle size, morphology, and agglomeration are very important since this influences mixing, and determines the surface contact area.

In this research, the goal was to determine the effect of different processing conditions to minimize the particle size and agglomeration. Different experimental variables were altered. These included reaction time, reaction temperature, starting materials, starting concentrations, and solution additives.

394. Analysis of SH-Containing Compounds Using DNBA

Katie Baxter, Department of Chemistry, Cleveland State University, Cleveland, OH

Many types of proteins have very low levels of aromatic amino acids which make conventional methods for quantifying proteins such as the Lowry and Bradford methods inaccurate. However, many proteins that have low levels of aromatic amino acids may contain high levels of sulfhydryl (SH) groups from cysteine. 5,5’ Dithiobis (2-nitro-benzoic acid) or DNBA is known to react with SH groups and produce a measurable change in absorbance in a stoichiometric manner. Theoretically, one mole of DNBA should react with one SH group on a thiol compound, creating a mixture of TNB ion (yellow in color) and one mixed disulfide ion. Therefore, we tested the use of DNBA using different SH containing compounds such as dithiotheitol, cysteine, glutathione (reduced), and glutathione (oxidized). The reaction with cysteine proceeded in the theorized stoichiometric manner, showing a steady increase in absorbance until a 1:1 ratio was obtained. Oxidized glutathione was used as a control because it contains only disulfide groups which do not react with DNBA, hence no reaction was observed. However, experiments with dithiotheitol and reduced glutathione demonstrated very different results with the saturation points well beyond the theorized values. This may indicate a different reaction mechanism taking place with these substances.

395. The Characterization of Natural Water Samples Collected From Diverse Sites In Central Ohio

Annie Nebergall, Derrick Kaseman, Alex Dotson and Ted M. Clark, Department of Chemistry, The Ohio State University, Columbus, OH

Natural water samples are well-suited for analysis in quantitative analysis chemistry courses, as a wide variety of analytes may be tested and different instrumental techniques are applicable. Within the current investigation, as part of the Research Experiences to Enhance Learning (REEL) program, water samples from diverse settings, e.g. rural areas and constructed wetlands, were collected and tested by student researchers. Methods of analysis included ion-selective electrodes for nitrate determination, spectrophotometric measurements for phosphate determination, and the on-site testing of dissolved oxygen levels. The wide range of student-generated research questions and their results will be discussed.

396. The Affect of Precipitation On the Concentration of Nitrogenous Species near Combined Sewage Overflows On the Olentangy River

Melanie Butler, Kelsey Kerton, Kimberly Shookman, Jennifer Yui and Ted M. Clark, Department of Chemistry, The Ohio State University, Columbus, OH

A student-led investigation of water quality near urban combined sewage overflow (CSO) sites has been undertaken as part of the Research Experiences to Enhance Learning (REEL) program. Within a 10-week quantitative analysis chemistry course at the Ohio State University, eleven water samples were collected from two sites on the Olentangy River, in Columbus, OH. The concentration of nitrogenous compounds was determined, along with conductivity, temperature, pH, water flow, and dissolved oxygen measurements. The concentrations of nitrate, nitrite, and ammonium ions, as determined by liquid ion chromatography, are reported for time frames both with, and without, precipitation occurring. Since precipitation during these periods did not result in sewer overflow at the CSO sites, these results provide insights into baseline values typical in the Fall for these analytes at two representative CSO sites.

397. A Short-Term Investigation of Combined Sewage Overflows (CSOs) along the Olentangy River

Andrew Goodrich, Daniel Hannah and Ted M. Clark, Department of Chemistry, The Ohio State University, Columbus, OH

The city of Columbus, OH employs a Combined Sewage Overflow (CSO) system to accommodate high water load in the sewers during periods of high precipitation. This system may ultimately lead to the disposal of sewage waste into local waterways and raises concerns regarding unhealthy levels of pollutants in these environments. As part of the Research Experiences to Enhance Learning (REEL) program, a student-led investigation of CSOs along the Olentangy River was undertaken in a quantitative analysis chemistry course at the Ohio State University. The goal of this study was to determine whether the CSO system presents a legitimate health concern to the inhabitants of the immediate area. The short-term (Fall season, 2008) impact of CSOs was examined by determining the concentration of multiple analytes, including nitrate, nitrite, phosphate, fluoride, and chloride. These species are common to waterways within the area and, when in excess, could detrimentally affect the local ecosystem. Our results suggest that, for periods of moderate precipitation, the CSO sites studied do not significantly contribute to increased pollutant levels and are therefore not negatively impacting the environment.

398. Isolation of Alpha-Mangostin In Garcinia Mangostana L

P. Lona Sharma[1], Rachel Kopec[2], Steven Schwartz[3], Clay Harris[1] and Ted M. Clark[1], (1)Department of Chemistry, The Ohio State University, Columbus, OH, (2)Department of Human Nutrition, The Ohio State University, Columbus, OH, (3)Department of Food Science & Technology, The Ohio State University, Columbus, OH

The mangosteen tree is a tropical evergreen indigenous to southern Asia. It has an edible fruit, Garcina mangostana L., and a bitter outer layer, or pericarp, plentiful in xanthones. This pericarp has long been used for medicinal purposes and remains significant in holistic eastern medicine. The isolation and characterization of xanthones in Garcina mangostana L. has importance since their anti-bacterial, anti-tumor, and anti-inflammatory properties are under investigation. As part of the Research Experience to Enhance Learning (REEL) program, an undergraduate researcher has studied the extraction of the xanthone alpha-mangostin by high performance liquid chromatography (HPLC). The use and optimization of various extraction procedures will be discussed.

399. Contamination of Urban Soils In the Greater Columbus, OH Area

Jason Stybel, Jason Eng, Steven Kiracofe and Ted M. Clark, Department of Chemistry, the Ohio State University, Columbus, OH

Anthropogenic activities in urban areas have the potential to concentrate potentially toxic materials, like lead and arsenic, in settings that often frequented by a large number of people. Exposure to these toxins poses numerous health risks, depending on the nature of the exposure. The goal of identifying areas with increased concentrations of harmful toxins should also be joined with efforts to establish baseline values for these same substances at sites with minimal anthropogenic contributions. To this end, more than 300 surface soil samples were collected throughout the Greater Columbus, OH area and analyzed by X-ray fluorescence spectroscopy by students in the Research Experiences to Enhance Learning (REEL) program at the Ohio State University. Sampling sites included urban parks (n=132), elementary schools (n=114), community gardens (n=26), and railroad tracks (n=17). Results indicate that approximately 10% of these samples have lead concentrations above the tolerable limit established by the World Health Organization of 100 ppm. The relationship between contamination level and anthropogenic activity will be discussed.

400. Inorganic Pigments (Project REEL)

Brian M. Urig, Ryan Hershey, Bryan Bernreuther, Paul Mason, Kurt Russell, Austin Smith, Mark Groseclose, Michael Shaffer, Becca Rugggear and Melissa Hubley, Science, Oxford High School, Oxford, PA, Oxford, PA

Inorganic Pigments (Project REEL)

From art work that is hundreds of years old to the modern finishes on automobiles, the use of colored pigments has played a major role in our society. As part of the Research Experiences to Enhance Learning (REEL) Program, students at Oxford Area High School investigated the nature of color in the Inorganic Pigments Module of REEL. In this high school adapted version, thirteen students synthesized various aqueous and solid compounds. Some of these compounds included solid sulfides, chromates, and molybdates as well as aqueous complexes of copper and cobalt. UV-Vis spectra were obtained for these materials, and the origin of color was determined based on the principles of molecular orbital theory. From these results, students will predict and/or justify the color of another set of compounds.

401. Ionic Liquid Crystalline Compounds of Transition Metals with Tetraalkylammonium Ligands

Elizabeth Jensen and Molly Soper, Department of Chemistry, Aquinas College, Grand Rapids, MI

A series of liquid crystal compounds of the general type bis(dimethyldioctadecyl)ammonium metal halide were synthesized using the metals Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Pt^{2+} and the halogens Cl or Br. Thermal analysis was done using differential scanning calorimetry and Mel-Temp methods in order to compare the members of the series to one another. It was determined that waters of hydration and oxidation state of the metals have less of an effect on the thermal properties than the identity of the halide.

402. The Synthesis of Re(CO)3+ Amino Acid Conjugates Using 2-Pyridine Carboxyaldehyde

Hira Qayyum and Christopher J. Ziegler, Department of Chemistry, University of Akron, Akron, OH

We are investigating rhenium(I) tricarbonyl complexes as models for new technetium imaging agents. In this poster, we report series of complexes for the generation of bifunctional chelating agents, and are using a new Schiff base method for the one-pot synthesis of a series of amino acid conjugates. The reaction of $Re(H_2O)_3(CO)_3^+$ with 2-pyridine carboxyaldehyde and amino acids results in the formation of complexes where the N-terminus forms a Schiff base coordinated to the metal. We have elucidated the structures of the glycine and alanine Schiff base conjugates, and the two compounds possess chiral dimeric structures. These compounds also exhibit a charge transfer transition in the visible region resulting from MLCT involving the 2-pyridine imine ligand. In addition, these complexes also show some fluorescence, which can potentially be used to image the localization of these complexes in cells.

403. Analysis of Snow Samples Collected in the Columbus Metropolitan Area

Michael Newman, Brandon C Balogh, Samuel Obuobisa and Myung Han, Department of Physical Science, Columbus State Community College, Columbus, OH

States of Indiana, Ohio, and Pennsylvania are leading the nation in the consumption of coal from their power plants. Acid rain is a harmful environmental effect of burning coal containing sulfur. Acidic rain falls in the Ohio River valley have been particularly noticeable (NADP, 2006). The SO_2 evinced from such combustion oxidizes in the atmosphere to produce SO_4 and then combines with H_2O to produce sulfuric acid. A set of snow samples was taken with random distribution in Columbus, Ohio for the prupose of determining relative levels of pollution and its distribution. These were then measured for conductivity, pH, particulate, and sulfate levels. No correlations were found due to the low number of samples but some valuable information was obtained. Overall, the data reflected the urban character of the samples collected, with the elevated sulfate and particulate levels reflecting the energy production of an industrialized nation. pH ranged from 4.05 to 8.3, with an average of 6.61 which is slightly less acidic than average rainwater. Conductivity ranged from about 5 to 150 micromho. Particulate levels were about 0.2 to 0.4 ppm. Sulfate levels for the subset of four samples were one to two orders of magnitude higher than the reported data obtained mostly from pristine polar or alpine locations. It remains inconclusive whether our sulfate data reflect urban character or contamination. Due to the pressing need for such data, and the known difficulty of its procurement, it is recommended that these studies be continued with greater rigor on a much larger scale with improved analytical tools.

404. A Possible Air Pollution Reducer and Source of Biodiesel: The Macroalgae Cladophora Gomerata

Johanna Dolch and Anthony Sky, Natural Sciences, Lawrence Technological University, Southfield, MI

I hope to combine two of my interests in this project and, in essence, kill two birds with one stone. Improving the world by reducing pollution and finding low cost alternative energy solutions to expensive foreign petroleum have been goals of mine for quite a long time. Excessive growth of cladophora in the Great Lakes has become a cause for concern that threatens to upset the delicate ecosystem of Michigan's Great Lakes. Because the Midwest is heavily polluted and also reliant on fossil fuels, I choose to study the effects of pollution on algae growth.

I am working with three professors, Drs. Nicole Villeneuve, Julie Zwiesler-Vollick and Anthony Sky. After consulting the scientific literature we hypothesize that algae growth may be affected by absorption of pollutants produced by combustion of fossil fuels. Furthermore, if air pollutants do feed the algae, determining the lipid content (percentage) of harvested algae will tell us whether or not macroalgae are a viable alternative fuel that can be converted to biodiesel.

405. Covalent Crosslinking of Thermoresponsive Polymer Nanoparticles

Kimberly C. Clarke and Clinton D. Jones, Department of Chemistry and Biochemistry, Mercyhurst College, Erie, PA

Hydrogel nanoparticles (microgels) have been researched for applications in medicine, biomaterials, and analytical techniques. N-Isopropylacrylamide (NIPAm) microgels respond to solution temperature changes by changing volume; concomitantly, there is a transition from a hydrophilic to a hydrophobic state with increasing temperature as the microgels shrink or swell, respectively. This property can be used to extract hydrophobic molecules due to favorable interactions between large organic molecules and the temperature-induced hydrophobic polymer. Such molecules interact with the microgels, extracting them from solution. As a proof of concept, experiments with fluorescent rhodamine and microgels have shown that a greater rhodamine concentration is extracted at a higher temperature versus extraction at a lower temperature. These results indicate a more favorable interaction between the rhodamine molecules and the microgels in a hydrophobic state. We are currently investigating the covalent linking of microgels to each other by reacting functional groups that have been incorporated onto the microgel surfaces with a linking molecule. We eventually plan to covalently attach microgels to PDMS coated SPME fibers. By extracting hydrophobic molecules with such a fiber, analyte extraction could be achieved without the use of large quantities of organic solvent. This would reduce the need for additional organic waste; a consequence of current extraction techniques.

406. Preparation and Study of the Optical Properties and Hydrophobicity of N-Isopropylacrylamide-Co-Styrene Microgel Colloidal Crystals

Richard J. Pompei and Clinton D. Jones, Chemistry and Biochemistry, Mercyhurst College, Erie, PA

We report on the synthesis of thermoresponsive polymer microgels with varying degrees of hydrophobicity for use in colloidal crystal assemblies. Microgels composed of `N`-isopropylacrylamide–`co`-styrene (pNIPAm-`co`–Sty) were synthesized via temperature-induced free-radical precipitation polymerization in aqueous solution. The crosslinker `N,N'`-methylene(bisacrylamide) was maintained at five mole percent in each case and the Sty monomer concentration was varied incrementally from zero to 10 mole percent. Each synthesis was performed under nitrogen gas at 70 ºC, and styrene monomer was added just prior to initiation. Particle diameter was determined in aqueous conditions using temperature controlled dynamic light scattering (DLS). Depending on the molar amount of styrene monomer used, particles ranged in diameter from 240 nm to 300 nm at 23 ºC. Colloidal crystal assemblies were constructed `via` temperature controlled centrifugation at 26 ºC and UV-vis spectroscopy was used to analyze Bragg diffraction exhibited by the resultant colloidal crystals. Results indicate that an increased hydrophobicity from the co-monomer stabilizes the colloidal crystal assemblies.

407. Development of Calcium, Fluoride, and Phosphorous Assays to Determine Tooth Enamal Demineralization

Kristin Donaldson and Peter J. Tandler, Department of Chemistry, Walsh University, North Canton, OH

Demineralization is the process when the mineral of the tooth structure, specifically calcium and phosphorous, are dissolved from the tooth’s enamel. In addition, fluoride can also be found in the tooth’s structure as fluoride treatments are used to increase the resistance to demineralization. The process of demineralization often leads to the formation of carious lesions. Bleaching, a process of lightening the tooth’s color with hydrogen peroxide is believed to cause demineralization of the tooth’s enamel. In order to determine if bleaching causes the demineralization of the tooth’s enamel, assays were developed to measure the concentration of calcium, fluoride, and phosphorous in a saliva matrix.

408. Pegylated Ethyl Malonate as a Solubilizing Ligand for Platinum(II) Antitumor Compounds

Pratik Chhetri, Bob A. Howell and Adina Dumitrascu, Center for Applications in Polymer Science and Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48859-0001, Mount Pleasant, MI

Organoplatinum antitumor drugs, principally cisplatin and carboplatin, have been broadly useful in the treatment of a variety of cancers, particularly those difficult to treat by other means. These drugs are also often used following surgical removal of tumors to assure that all vestiges of the disease are destroyed. While these compounds are very effective, broad spectrum cancer drugs, their administration may be accompanied by very severe side effects. The most debilitating of these are kidney toxicity and extreme nausea. A way to diminish or avoid the side-effects is to administer a formulation in which the active platinum moiety is covalently bound to a biocompatible, water-soluble polymer as carrier. Slow release of the active platinum species in the extracellular fluid could keep its concentration below that necessary to cause side effects. A very good method to accomplish this has been to attach (1,2-diaminocyclohexane)platinum(II) moieties to the surface of a generation 4.5 PAMAM dendrimer. About forty platinum units can be placed on the dendrimer and the release profile for platinum species is well-behaved. However, the dendrimer is quite expensive and it is desirable to have a carrier vehicle that is more readily available at lower cost. Attaching poly(ethylene glycol) units to a dicarboxylate ligand may generate such carrier.

409. Qualitative and Quantitative Analyses of Proteinaceous Binders in Rock Paintings

William Malcolm, Geneve Maxwell and Ruth Ann Armitage, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI

There are many existing forms of archaeological rock art found in the southwest region of North America and Central America. We have been using thermally-assisted hydrolysis/methylation-gas chromatography-mass spectrometry (THM-GC-MS) to characterize the organic materials found in the paint samples. Using THM-GC-MS for the analyses, it has appeared that amino acids may be present in some of the paint samples. It is believed that these amino acids may be residues from the proteinaceous binders used in the paint. Extraction, hydrolysis, and derivatization of these amino acids to their N(O,S)-ethoxycarbonyl ethoxy esters and analysis by GC-MS were used to further characterize the nature of the proteinaceous material, and to determine their relative concentrations in the paint and substrate rock. The goal of this study is to determine the composition of the binders in rock art samples that are to be or have been dated using the plasma-chemical oxidation and accelerator mass spectrometry technique, and develop an effective method for the removal of inorganic salts while preserving the organic matter in the binders. Ultimately, this work will aid archaeologists who study rock paintings in understanding both the age and composition of these unique artifacts.

410. Detection of DDT in the Environment: Water Analyses Using Solid-Phase Extraction and Gas Chromatography-Mass Spectrometry

Caitlin Van De Car and Ruth Ann Armitage, Department of Chemistry, Eastern Michigan University, Ypsilanti, MI

The purpose of this project was to evaluate the efficiency of environmental analyses in an undergraduate analytical chemistry classroom. In winter 2008, students in the NSF-funded Creative Scientific Inquiry Experience (CSIE) Quantitative Analysis course analyzed local water samples for trace quantities of DDT and its metabolites using solid-phase extraction (SPE) and gas chromatography-mass spectrometry (GC-MS). Unfortunately, the results were inconclusive as no DDT or its metabolites were detected in the samples, even using selected ion monitoring. One of the themes of the course was how human activity in the past can still be detected in the modern environment. This project carried on the work from the course, attempting to develop a classroom-appropriate method that would introduce students to using GC-MS to measure residues of this long-banned pesticide.

411. Methanolysis Reactions of N-Acylhydrazides Using Polymer Supported Acids

Caitlin McCurdy-Robinson[1], Matthew Tricomi[1], Eric Fichtenbaum[2], Samuel Boayke[1], Nataliya Isakov[1], Dustin Baker[1], David Johnson[1], David J. Hart[1] and Christopher Callam[1], (1)Department of Chemistry, The Ohio State University, Columbus, OH, (2)Department of Chemistry, Ohio State University, Columbus, OH

Acylhydrazides have been used in a variety of organic reactions including ortho-metallation reactions and as intermediates in the preparation of aminimide based drag reducing agents., however their synthetic conversion to more useful carboxylic acids or methyl ester derivatives is often difficult. The literature also reports a number of exotic methods for the hydrolysis of acylhydrazides : (Pb(OAc)4, MnO2, HIO4, CuCl2, and PhI(OH)OTs.) All of which involve reactions that are initiated by oxidation of the basic nitrogen (N(CH3)2). We have prepared a small library of fourteen different acyl acylhydrazides by treatment of the corresponding acid chloride with either dimethyl hydrazide or 4-amino morpholine. We report here-in a direct method for the conversion of acylhydazides to methyl esters under non-oxidative conditions. The direct methanolysis of a small library of acylhydrazides using DOWEX-50 as an acid promoter in methanol has been investigated and the initial studies performed yielded the corresponding methyl ester in good to excellent yield. All compounds were characterized by NMR, IR and GC.

412. Subcloning the Danio Rerio Peptidylarginine Deiminase II (PAD2) Gene Into the Pet/D-TOPO® Expression Vector

Zachary Brodnik and Diana N. Barko, Department of Chemistry, Baldwin-Wallace College, Berea, OH

The peptidylarginine deiminase II (PAD2) enzyme catalyzes the conversion of arginine residues to citrilline. Citrillinated proteins, including the myelin basic protein, suggest a mechanism for the effects in diseases such as Multiple Sclerosis (MS). The PAD2 enzyme has been proposed to be in excess in MS patients yet little is known about the enzymatic mechanism. In order to understand the role of PAD2 in zebrafish we have designed a project where we will express, purify, and kinetically characterize the enzyme (PAD2) `in vitro`. Specifically the PAD II gene from `Danio rerio` will be subcloned in the pET/D-TOPO® expression vector. This project has focused on the PCR reaction to generate the insert for the pET/D-TOPO® vector. The primers and PCR reaction conditions are currently being optimized to generate the PAD2 insert from the PME18S-FL vector. When successful, the PAD2 insert will be TOPO® cloned into the pET/D-TOPO® expression vector and transformed into competent `Escherichia coli` cells.

413. N(epsilon)-Thioacetyllysine-Containing Human SIRT2 Enzyme Inhibitors: a Structure-Activity Study

Shayna Robinson, Undergraduate, Brett M. Hirsch, Nuttara Jamonnak and Weiping Zheng, Department of Chemistry, University of Akron, Akron, OH

Silent information regulator 2 (Sir2) enzymes are a family of evolutionarily conserved protein deacetylases that can catalyze the nicotinamide adenine dinucleotide (NAD^+)-dependant protein lysine N(epsilon)-deacetylation reaction. In humans, five Sir2 homologs possessing the protein deacetylase activity, i.e. SIRT1-3 and SIRT5-6, have been identified. Human SIRT2-catalyzed deacetylation reaction is currently regarded as a novel therapeutic target for developing anti-Parkinson's disease drugs since genetic and pharmacological inhibition of SIRT2 activity were previously shown to be able to rescue the alpha-synuclein-mediated cytotoxicity and to protect against dopaminergic cell death. Built upon our previously discovered potent and selective N(epsilon)-thioacetyllysine (ThAcK)-containing lead peptide inhibitor for human SIRT2, and toward developing peptidomimetic/non-peptide inhibitors, we performed a structure-activity study on the lead peptide inhibitor. We found that (i) ThAcK-containing pentapeptides still maintained the potent SIRT2 inhibition exhibited by the ThAcK-containing 9-amino acid lead peptide inhibitor; (ii) all the four positions (i.e. the -2, -1, +1, and +2 positions) immediately flanking the ThAcK warhead in the pentapeptide lead inhibitor could be substituted with alanine without sacrificing the SIRT2 inhibitory potency. While the newly discovered potent short peptide inhibitors may find their own use as the functional probe for human SIRT2 enzyme, the results from the current study have laid a foundation for our ongoing efforts toward transforming peptidic into peptidomimetic/non-peptidic SIRT2 inhibitors.

414. N(epsilon)-Thioacetyllysine-Containing Human SIRT1 Enzyme Inhibitors: a Structure-Activity Study

Caroline A. Gallo, Undergraduate, Brett M. Hirsch and Weiping Zheng, Department of Chemistry, University of Akron, Akron, OH

Silent information regulator 2 (Sir2) enzymes are a family of evolutionarily conserved protein deacetylases that can catalyze the nicotinamide adenine dinucleotide (NAD^+)-dependant protein lysine N(epsilon)-deacetylation reaction. In humans, five Sir2 homologs possessing the protein deacetylase activity, i.e. SIRT1-3 and SIRT5-6, have been identified. Human SIRT1-catalyzed deacetylation reaction constitutes a potential therapeutic target for developing novel anti-cancer drugs since genetic and pharmacological inhibition of SIRT1 activity were previously shown to be able to confer anti-proliferative effects. Built upon our previously discovered potent and selective N(epsilon)-thioacetyllysine (ThAcK)-containing lead peptide inhibitor for human SIRT1, and toward developing peptidomimetic/non-peptide inhibitors, we performed a structure-activity study on the lead peptide inhibitor. We found that (i) ThAcK-containing pentapeptides still maintained the potent SIRT1 inhibition exhibited by the ThAcK-containing 18-amino acid lead peptide inhibitor; (ii) three of the four positions (i.e. the -2, -1, +1, and +2 positions) immediately flanking the ThAcK warhead in the pentapeptide lead inhibitor could be modified (e.g. with alanine substitution) without dramatically sacrificing the SIRT1 inhibitory potency. While the newly discovered potent short peptide inhibitors may find their own use as the functional probe for human SIRT1 enzyme, the results from the current study have laid a foundation for our ongoing efforts toward transforming peptidic into peptidomimetic/non-peptidic SIRT1 inhibitors.

415. Probing the Role of Gag in Regulation of HIV Reverse Transcription

Andrew Goodrich, Christopher P. Jones and Karin Musier-Forsyth, Department of Chemistry, The Ohio State University, Columbus, OH

Human immunodeficiency virus (HIV) relies heavily on nucleic acid chaperone proteins at critical steps throughout its life cycle. A retrovirus, HIV enters a host cell and reverse transcribes its RNA genome into DNA, which is integrated into the host DNA for the production of new viral RNAs and proteins that assemble at the plasma membrane. The poly-protein Gag, which consists of the matrix, capsid, and nucleocapsid (NC) domains, directs virus assembly and packages the RNA viral genome into new virions. Evidence suggests that Gag, a chaperone protein, is also responsible for annealing of the $tRNA^{Lys}$ primer to the HIV genome, the first step of reverse transcription. After virus budding, however, Gag is proteolyzed, and freestanding NC assumes the role as the chaperone for reverse transcription and integration. Although both Gag and NC promote $tRNA^{Lys}$ annealing `in vitro`, the next step of reverse transcription, extension from the primer by reverse transcriptase, is inhibited by Gag. Interestingly, `in vivo` studies have found that virus variants with specific NC domain mutations undergo premature reverse transcription, which causes the packaging of DNA and abolishes infectivity. In this work, these Gag variants were tested for their ability to aggregate and bind nucleic acids, key functions of chaperone proteins, and to facilitate tRNA annealing and reverse transcription `in vitro`. We show that the chaperone activity of these variants is robust and propose an explanation for Gag's role in inhibiting reverse transcription as well as how critical residues in NC contribute to Gag's chaperone activity.

416. Synthesis of Cholesteryl Esters for Use as Standard in Renal Cell Carcinoma Research

Jennifer K. Razek, Leeanne R. Taylor, M. James Ross and Jody M. Modarelli, Department of Chemistry, Hiram College, Hiram, OH

Cholesterol esters are formed by the esterification of cholesterol with long-chain fatty acids such as oleic and linoleic acids. They are the means by which cholesterol is transported through the blood by lipoproteins and cholesterol accumulates in the cell. Total cholesterol and cholesterol esters increases in Renal Cell Carcinoma (RCC) tissue by 8-fold and 35-fold, respectively. To date, no circulating tumor markers have been identified for RCC. Detecting lipid metabolites in the urine of patients with RCC represents a novel approach to cancer biology. Accurate measurement of the different cholesterol esters in biological sample requires a synthetic method that is rapid, gives a high yield and distinguishes with high purity individual esters. The research reported here outlines a method for the synthesis of an oleic and linoleic acid standard as a means of measuring cholesterol esters in biological sample.

417. S-Glutathionylation in HEK 293 Cell

Yuh-Cherng Chai, Jasen Lee Gilge and Michael Fisher, Department of Chemistry, John Carroll University, University Heights, OH

Cellular molecules possess various mechanisms in responding to oxidant stress. In terms of protein responses, protein S-glutathionylation is a unique post-translational modification of protein reactive cysteines forming disulfides with glutathione molecules. This modification has been proposed to play roles in antioxidant, regulatory and signaling in cells under oxidant stress. In this report, specific S-glutathionylated proteins were demonstrated in human embryonic kidney 293 cells treated with two different oxidative reagents: diamide and hydrogen peroxide. Under the experimental conditions, these two oxidants decreased glutathione concentration without toxicity. We further show the effect of alteration of the cellular thiol pool on the amount of protein S-glutathionylation. Cellular thiol concentrations were altered either by a specific way using buthionine sulfoximine, a specific inhibitor of glutathione biosynthesis or by a non-specific way, incubating cells in cystine-methionine deficient media. Cells only treated with either buthionine sulfoximine or cystine-methionine deficient media did not induce protein S-glutathionylation, even though both conditions decreased 65% of cellular glutathione. Moreover, the amount of protein S-glutathionylation under both conditions in the presence of oxidants was not altered when compared to the amount observed in regular media with oxidants present. Protein S-glutathionylation is a dynamic reaction which depends on the rate of adding and removing glutathione. Phenylarsine oxide, which specifically forms a covalent adduct with vicinal thiols, was used to determine the possible role of vicinal thiols in the amount of glutathionylation. Our data shows phenylarsine oxide did not change glutathione concentrations, but it did enhance the amount of glutathionylation in oxidant-treated cells.

418. Chemical Control of Seed-Layer Grown ZnO Nanorod Arrays

Andrew J. Pohlman and Simon P. Garcia, Department of Chemistry, Kenyon College, Gambier, OH

Zinc oxide films containing arrays of nanorods were grown from aqueous solution. Seed layers were deposited on hydroxylated silicon substrates by a variety of methods, including immersion in solutions of nanocrystals and spin coating of a sol-gel precursor. After annealing to ensure adhesion, crystals were then grown on the seed layers using pH-controlled crystallization of zinc oxide from solution. The resulting films were imaged by scanning electron microscopy to evaluate three characteristics: (a) size of individual crystals, (b) spacing of crystals, and (c) orientation of crystals with respect to the substrate. Comparison of films with different seed layers showed that crystals are oriented perpendicular to the substrate when the spacing is small, while crystals are tilted when the spacing is large.

419. Selective Synthesis of An α-Ellagitannin

Klaus B. Himmeldirk and **Amanda L. Radune**, Department of Chemistry & Biochemistry, Ohio University, Athens, OH

The first synthesis of the natural product 1,2,3-Tri-O-galloyl-4,6-O-[(S)-4,4',5,5',6,6'-hexahydroxydiphenoyl]-***α***-D-glucopyranose is shown. The selective formation of the α-epimer could be achieved by using a recently established protocol for the formation of α-esters of glucose. The cyclic lactone with benzyl group protected 4,4',5,5',6,6'-hexahydroxydiphenic acid did not form when the (R)-enantiomer was employed.

420. Analysis of Lake Erie and Maumee River Water for Nitrate

Matthew J. Zielinski, student, Robert A Taylor and Kurt T Schroeder, Department of Chemistry, Bowling Green State University, Bowling Green, OH

Water Analysis for Nitrate Ion

This poster describes the experiment examining the different levels of nitrate, NO_3^-, found within local bodies of water. High Nitrate levels in drinking water pose danger to humans. The EPA has set the Maximum Contaminant level (MCL) for Nitrate in drinking water at 10 ppm.

In Bowling Green, Ohio, Maumee River serves as the source of drinking water. This river flows through an agricultural area and is one of the major tributaries to Lake Erie. The possibility of fertilizer runoff causing elevated Nitrate concentrations in both Maumee River and Lake Erie is fairly high. Thus, the water samples researched were taken from Lake Erie in two separate locations (at Overlook Beach Park in Mentor Ohio, and at a beach located outside Toledo) as well as from Maumee River at a park south of Perrysburg on Rt. 65 between Grand Rapids and Waterville.

In the analytical procedure used, the concentration of Nitrate (as ppm of Nitrogen) was determined using a Nitrate Ion-Selective Electrode (ISE) that develops a potential (voltage) that changes with the concentration of Nitrate in solution. The potential of nitrate ISE changes with the dissolved nitrate concentration but is insensitive to concentrations of any other ions that may be in solution. A set of standard solutions having known nitrate concentrations was prepared. By comparing the measured responses of an environmental water samples to those of the standards, the concentrations of Nitrate in the environmental samples was found.

421. Solution Luminescence From Chloro(2,2':6',2" terpyridine) Platinum (II) in Anionic Micelles

Abigail Van Wassen, Natalie A. Larew and Scott D. Cummings, Department of Chemistry, Kenyon College, Gambier, OH

For Pt(II) complex cations of the type $[Pt(terpy)X]^{n+}$, where terpy = 2,2′:6′,2″-terpyridine, luminescence depends strongly on the nature of the ancillary ligand X. Although a growing number of complexes in this family are luminescent in fluid solution, no room-temperature luminescence has been reported for the "parent" chloro complex $[Pt(terpy)Cl]^+$ in water or organic solvents. This lack of solution luminescence has been explained in terms of rapid deactivation of the low energy metal-to-ligand charge transfer (MLCT) excited state, caused by two effects: collisional quenching by solvent, and non-radiative decay involving a thermally-accessible metal centered (MC) excited state.

We have discovered two types of luminescence not previously reported for $[Pt(terpy)Cl]^+$ in room temperature aqueous solution: (1) ^{3}MLCT phosphorescence from cation monomers in anionic micelles, and (2) luminescence from aggregates in concentrated aqueous solution or in solutions having surfactant concentrations below the critical micelle concentration. The related phenylacetylide complex cation $[Pt(terpy)(CCPh)]^+$ displays comparable luminescence enhancement in SDS micelles.

422. Analysis of Natural Water Samples for Nitrate

T.A. Sojka, Student and Desirea D. Scott, Student, Department of Chemistry, Bowling Green State University, Bowling Green, OH

Analysis of natural water samples for Nitrate

The purpose of this experiment is to compare the differences between in Nitrogen, particularly in the form of Nitrate, NO_3^-, in water sources as the Maumee River flows through fields that are treated with fertilizers containing Nitrogen, as these contaminants can have a major effect on algae growth in the rivers, reducing the Oxygen concentration, as well as having an effect on infants if they ingest certain levels of Nitrogen. The water samples were gathered from two specific points along the Maumee river, hoping to support our hypothesis that samples, both river water and tap water, taken from a distance upstream, would contain less Nitrogen than samples taken from the downstream location. Samples of the Maumee River and a sample of tap water nearby at two locations along the Maumee River, Defiance Ohio, and Toledo Ohio were taken. The two sample areas were about 60 miles apart, insuring enough distance for the river to have a change in Nitrogen, if there was to be one.

The concentration of Nitrate ion was determined using a Nitrate Ion Selective Electrode (ISE), which develops voltage corresponding to Nitrate ion concentration. The relationship between voltage and Nitrate concentration is described by the following equation Voltage=m X log(nitrate) + b. This relationship was established by using standard solutions with known nitrate concentrations. The potentials developed in natural samples were then compared to those of standards.

423. Analysis of Tuscarawas River Water for Nitrate Ion Concentration: A REEL Undergraduate Research Project

Jenna N. Hilty, Kristine A. Lahman, Hannah R. Mason, Marissa K. Snyder and Jens M. Hemmingsen, Department of Chemistry, Capital University, Columbus, OH

Nitrate ion (NO_3^-) is a nutrient pollutant found in waterways near agricultural, industrial, and sewage waste areas. If consumed, concentrations in excess of 10 ppm can cause illness in children under the age of six months. Samples from the Tuscarawas River were taken near the Newcomerstown Waste Water Treatment Plant. Using an ion selective electrode and a standard addition method, these water samples were analyzed for NO_3^- concentration. Data show a NO_3^- concentration range of 0 to 1.377 downstream and a range of 0-5.160 upstream. These results suggest contamination from the waste water treatment plant. At the point source where waste is released into the water, NO_3^- concentration ranges from 0 to 7.699 ppm. This concentration is not harmful to humans if consumed. This project was performed in the general chemistry laboratory at Capital University as a part of the Research Experience to Enhance Learning (REEL) consortium. Three weeks of the course were devoted to quantitative analysis of ions in natural water samples.

424. Analysis of Maumee River Water for Nitrate

Ashley N. Thompson, student, Department of Chemistry, Bowling Green State University, Bowling Green, OH

Water Analysis for Nitrate Ion

Water quality is a major priority for public health authorities, specifically in Northwest Ohio. Because of high amounts of agriculture in this region there is high risk for water contamination caused by agricultural runoff. One way to measure if water is affected by high levels of agriculture is to analyze water from Maumee River, which is the major water source throughout the region. It supplies drinking water to many areas in Northwest Ohio.

To analyze differences in nitrate concentrations along the Maumee River two samples were taken, one from Maumee Bay State Park, and another from downtown Perrysburg, Ohio. The third sample was taken from bottled water. The treatment of the bottled water is unknown because it this information was not given on the packaging. Nonetheless, since this water is distributed for drinking, it should have low enough concentration of Nitrate for safe drinking.

The method used to determine Nitrate ion concentration was based on the measurement of voltage that develops across a membrane in Nitrate Ion Selective Electrode (ISE). This voltage is dependent on NO_3^- concentration and is not influenced by other ions' concentrations. A series of standard solutions with known Nitrate concentrations was prepared and the voltages found for these standards were compared to those found for the environmental samples.

425. Molecules as Models: Light Harvesting Devices

Brian J. Yeager, Emmy Lou Dickinson, Kristin Hom, M. James Ross, Maria Sember, Robyn Phillips, Divya Balasubramanian, Cara Citraro and Carol D. Shreiner, Department of Chemistry, Hiram College, Hiram, OH

Arborols are well known for their ability to form stable, reversible gels in aqueous solution. Our strategy aims to employ the water soluble properties of arborols in conjunction with the tunable redox, absorption and emission properties of transition metal bis-terpyridyl complexes in order to form a water soluble, stable gel complex. The synthesis and characterization of the complex is described. The ability of the gel to perform as a potential light-harvesting complex with a suitable energy partner is also under investigation.

426. The Buzz On Chocolate

Jennifer Ashley White and Susan Sonchik Marine, Ph.D., Department of Chemistry and Biochemistry, Miami University Middletown, Middletown, OH

Chocolate is concocted from cocoa powder, cocoa butter, sugar, and milk powder with great variations possible in the products. An excess of chocolate can stimulate the central nervous system much as coffee does. Two chemical components of interest in chocolate are caffeine and theobromine. An HPLC analysis was developed to determine the concentrations of each in chocolate containing 20-72% cocoa powder. The correlation of theobromine concentration with cocoa content will be shown. Low levels of caffeine and high levels of theobromine were found. While theobromine has one tenth the effect of caffeine as a stimulant, it is present in much greater quantities in the chocolate and is probably responsible for the buzz caused by an excess of chocolate.

427. Investigation of Kinetic and Mechanistic Aspects of the Corey-Winter Olefination

Derek M. Dranichak, Travis L. Dill, Amanda-Lynn Warner, John A. Wolf, Amanda S. Wriston and Timothy L. Troyer, Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV

Our desire to develop short and efficient syntheses of bioactive substances has led us to investigate the Corey-Winter olefination reaction in more detail. Despite its widespread use in the synthesis of complex organic molecules, there exists no consensus on the exact intermediates involved in the reaction. Some evidence suggests a dioxacarbene is involved. We believe this dioxacarbene could be a useful reactant that can be utilized in novel reactions. The dioxacarbene, if present, is likely affected by the steric and electronic nature of the molecule it is a part of. There is no thorough study reported to date on stereoelectronic effects in the Corey-Winter olefination. We have focused initially on the elimination of dihydroxy phenylpropanes. The products of this elimination were predicted to have higher boiling points as well as being easily identified by standard spectroscopic methods. The dihydroxy phenylpropanes were synthesized by Wittig olefination with benzaldehydes followed by a one pot epoxidation – ring opening hydrolysis. The resulting diols were then converted to both cyclic carbonates as well as cyclic thiocarbonates which could then be studied for their rate and yield in the Corey-Winter olefination.

428. Effect of pH On Nitrate Levels in Scioto River

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This REEL project evaluated the effect of pH on nitrate levels in water samples taken from Scioto River along the Scioto Park in Dublin, Ohio. Nitrate is a major contaminant in streams, especially in spring due to fertilizer application on farms along the waterways.

In natural state, and under limited oxygen levels denitrification occurs:

NO_3^- to NO_2^- to NO to N_2O to N_2

In the initial February samples, the nitrate level was 5.7 mg/L. With the levels of pH adjusted, the nitrate levels were 0.8 mg/L, 3.7 mg/L, and 4.6 mg/L at pH = 5.0, pH = 6.0, and pH = 7.0 respectively. Lower pH values seemed to be associated with a greater removal of nitrate from the water samples. Early spring samples show a similar trend, though the values do not seem to be as widely apart as compared with the winter samples.

429. Negative Thermal Expansion Materials in the $A_2Mo_3O_{12}$ Family with Mixed Site Occupancy

Shannon K. Kraemer and Cora Lind, Associate Professor, Department of Chemistry, The University of Toledo, Toledo, OH

This project is exploring new negative thermal expansion (NTE) materials. There is an interest in these materials because when mixed with materials that have positive expansion, they could create composites with zero thermal expansion. The main family of interest for this project is the $A_2M_3O_{12}$ family; where A = trivalent metal and M = W or Mo. These materials usually form a monoclinic phase at lower temperatures and an orthorhombic phase at higher temperatures. The orthorhombic structure is the only phase known to display NTE. The expansion and phase transition behavior depend strongly on the cations incorporated into the structure. For this project only Mo was used for the M site. The A site was substituted by a mixture of $In^{3+}$and Ga^{3+}, with $InGa(MoO_4)_3$ as the target compound. The samples were prepared using non-hydrolytic sol-gel chemistry, and characterized by thermal analysis and powder X-ray diffraction. Synthesis conditions were varied to obtain homogeneous $InGa(MoO_4)_3$ samples.

430. Microwave-Accelerated Halide-Catalyzed Cycloaddition Between Glycidyl Ethers and Isocyanates

Nivhan Arumugasamy, Shannon K. Kraemer, **Amanda J. Lodzinski**, Aileen N. Newmyer, Rommel S. Talan and Steven J. Sucheck, Chemistry, The University of Toledo, Toledo, OH

Undergraduate organic chemistry laboratory students at the University of Toledo conducted a mini-research project over a three period module related to the chemistry of N-aryloxazolidinones. The N-aryloxazolidin-2-one moiety is present in a number of compounds which show diverse biological activities. Some of their properties include monoamine oxidase inhibition and antibacterial activity. Due to this medicinal importance, methods for generating libraries of these compounds have been of continued interest. Students used a microwave accelerated halide-catalyzed cycloaddition between an arylisocyanate and a t-butylglycidyl ether to generate a previously unknown C5-substitued aryloxazolidinone. The product could be formed in good yield by irradiation (300W) for 20 minutes maintained at 150 °C. The expected product was identified by analysis of the crude reaction by NMR and ESI-MS.

431. Exploring Halide Catalysts in a Microwave-Accelerated Cycloaddition Between Epoxides and Isocyanates

Evan A. Bruneau, Bret N. Feirstine, Jesse J. Monroe, Julia F. Mucci, Charles M. Oliver, **Ngam Sy**, Rommel S. Talan and Steven J. Sucheck, Chemistry, The University of Toledo, Toledo, OH

Undergraduate organic chemistry laboratory students at the University of Toledo conducted a mini-research project over three lab periods on use of different halide salts in a microwave-accelerated halide-catalyzed cycloaddition between tolylisocyanate and epibromohydrin. Students found that the catalyst tetrabutylammonium bromide (1%) in xylenes with irradiation (300W) for 20 minutes at 150 °C produced the desired N-aryloxazolidin-2-ones in 70-80%. In contrast, a limited attempt to use 1% CuI in methyl sulfoxide overheated under the same conditions in as little as two minutes. Only isocyanate-derived urea-based products could be identified from the latter experiment.

432. Water Analysis for Nitrate

Brian C. Gulko, student, Alexandra M Klinchenko and Brenden P Jenks, Department of Chemistry, Bowling Green State University, Bowling Green, OH

Water Analysis for Nitrate

Nitrate ion is a common pollutant in public drinking water. Elevated Nitrate levels can have detrimental effects to young infants and the elderly. A study to measure the nitrate levels in various sources of potable water for the Bowling Green community is described.

The samples of water were obtained 5 miles apart from each other from the Maumee River in Waterville, Ohio. Water from this location is sent to Bowling Green to a water treatment plant for consumer use. Samples of Bowling Green tap water as well as Dasani bottled water were analyzed as well.

The procedure used for Nitrate analysis utilized Nitrate Ion Selective Electrode (ISE) which measures potential developed across a membrane, which is related to NO_3^- concentration. Using Standard solutions with known Nitrate concentration, a Calibration graph was prepared and used to determine the concentration of Nitrate in samples being investigated.

Levels of nitrate in Maumee River water were near the safe maximum of 10 mg of Nitrogen per Liter of water. The lowest nitrate levels in Dasani tap water indicate that Dasani's source of water may be less susceptible to nitrates from farm pollution or other contaminants.

433. Isomerization of Itaconic Anhydride to Citraconic Anhydride by Dimethyl Sulfoxide

Kyle E. Hart, Student and Jack Williams, Department of Chemistry and Biochemistry, Mercyhurst College, Erie, PA

Citraconic anhydride is a product of increasing demand in industry. It has for several decades formed the subject of much research in order to define the most economical processes for its manufacture. The isomerization of itaconic anhydride to citraconic anhydride has been recorded using amines as a catalyst, or using organic catalysts (pKa between 4 and 10). Dimethyl sulfoxide (DMSO) is an important polar aprotic solvent, and somewhat acidic (pKa=35). To see if DMSO will isomerize itaconic anhydride, spectra of a saturated solution of itaconic anhydride (DMSO, and TMS) were obtained at intervals (immediately, one week, two weeks, and three weeks) on a room temperature sample, which were compared to a control sample without DMSO. The ratio of the concentration of itaconic anhydride to citraconic anhydride gradually increased with respect to time; therefore, a successful partial isomerization was completed with only DMSO in itaconic anhydride. A proposed mechanism closely resembles that for diethyl malonate, which is well documented.

434. Oxidation of Primary and Secondary Alcohols by 4-Acetylamino-2,2,6,6-Tetramethylpiperidine-1-Oxoammonium Tetrafluoroborate In Aqueous Media

Phillip R. Sharrow and Matthew R. Luderer, Department of Natural Science, Mathematics, and Engineering, University of Pittsburgh at Greensburg, Greensburg, PA

The water soluble oxidant, 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate, has been found to oxidize a variety of aliphatic and aromatic primary and secondary alcohols to their corresponding aldehydes and ketones with and without catalyst in aqueous media in good to excellent yields.

435. Preparation of Enaminones From 1,3-Diones Using Ammonium Acetate In Aqueous Media

Jake Lorence, Phillip R. Sharrow and Matthew R. Luderer, Department of Natural Science, Mathematics, and Engineering, University of Pittsburgh at Greensburg, Greensburg, PA

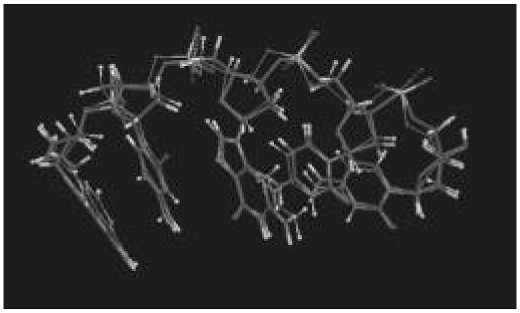
An environmentally friendly method for the preparation of enaminones from 1,3-diones using ammonium acetate in aqueous media has been developed.

436. Quantum Mechanical (MNDO and 3-21G*) Studies of the 2-D NMR-Derived Structures of the N-Terminal Zinc Finger of the HIV-1 Nucleocapsid Protein Complexed with the Psi-Site Analog, dACGCC (PDB Entries: 1HVO and 1HVN)

Salvatore Profeta Jr., **Berhanemeskel A. Nida, Student** and David Everson, Department of Chemistry and Biochemistry, DePauw University, Greencastle, IN

A synthetic peptide with the sequence of the N-terminal CCHC (CCHC = **Cys-X,-Cys-X4-His-X,-Cys; X**=variable AA) zinc finger of the HIV nucleocapsid protein, Zn(HIV1-Fl), has been studied using 2D-NMR by South and Summers (Protein Science (1993) **2**, 3-19). Titration of Zn(HIV1-Fl) with different nucleotide sequences revealed sequence dependent binding involving at least one guanosine residue for tight complex formation to the HIV-1 psi-packaging signal, d(ACGCC). The 2D-NMR enabled three-dimensional modeling of the complex. To evaluate deformation of the A-helical nucleotide strand, SPARTAN idealized models were built, and compared to that observed (figure below). We report relative conformational energies from MNDO and 3-21G* calculations on the fifteen protein structures in the PDB entries, 1HVN and 1HVO. Graphical representations of the electrostatic potential (ESP), LUMO & HOMO orbitals, are presented together with the structures' relative energies. Constrained molecular mechanics minimizations were performed to relieve extreme contacts created by the NMR analysis. MNDO calculations suggest a range of >50kcal/mol across the 15 conformations; 3-21G* calculations assess the range at ~21 kcal/mol, consistent with the latter method's superior treatment of electrostatics and hydrogen bonding.

Superposition of the observed A-DNA fragment in 1HVN and the ideal d(ACGCC) from SPARTAN.



437. Light-Induced Degradation of the Pharmaceutical Salbutamol in Aqueous Solutions

Leah G. Dodson, undergraduate and Carlos E. Crespo-Hernandez, Department of Chemistry, Case Western Reserve University, Cleveland, OH

Recent concerns over the presence of pharmaceuticals in drinking water and natural water sources have prompted evaluations of not only the potential health risks associated to the constant intake of minute amounts of these compounds by living organisms, but also concerning the environmental fate of these pharmaceuticals in the environment. Salbutamol, also known as Albuterol, is a pharmaceutical compound commonly used to relieve bronchial spasms associated with asthma. Several studies have detected Salbutamol in natural water sources worldwide in concentrations as high as 471 ng L^{-1}. Salbutamol exists in aqueous solutions as an equilibrium mixture of four different species: the radical cation, the zwitterionic form, the uncharged specie, and the anionic radical. Sunlight degradation of Salbutamol may be responsible for contributing new products to the already polluted waters. In this work, we used Xe-lamp irradiation; UV-vis and fluorescence spectroscopic techniques, as well as high performance liquid chromatography, to show that light-induced degradation of Salbutamol forms at least seven products, some of which absorb at longer wavelengths than the parent compound. Experiments at different pH conditions further show that Salbutamol is sensitive to light absorption in all pH conditions. However, the degradation rate is faster at pH 3 and 12, suggesting that the cationic and anionic species should be the most reactive to sunlight.

438. A Structurally Characterized Series of 1,1,3,3-Tetramethylguanidine Solvated Magnesium Aryloxide Complexes

Jessie Monegan and Scott D. Bunge, Department of Chemistry, Kent State University, Kent, OH

The synthesis and structural characterization of several novel 1,1,3,3-Tetramethylguaindine (H-TMG) solvated magnesium aryloxide complexes are reported. Bu_2Mg was successfully reacted with H-TMG, $OC_6H_3(CMe_3)_2$-2,6 (DBP), and either an alcohol, or an acid in a 1:1 ratio to yield the corresponding $[Mg(\mu\text{-}L)(DBP)(H\text{-}TMG)]_2$ where L= OCH_2CH_3 (OEt), $O_2CC(CH_3)_3$ (OBc), or $O_2C(C_6H_2$-2,4,6-$CH_3)$ (TMBA). Bu_2Mg was also reacted with a 1:2 ratio with H-TMG and $OC_6H_3(CMe_3)$-2-(CH_3)-6 (BMP) to yield the corresponding $[Mg(BMP)_2(H\text{-}TMG)_2]$. These compounds were characterized by single-crystal X-ray diffraction. The bulk powders for all complexes were found to be in agreement with the crystal structures based on elemental analyses, FT-IR spectroscopy, and ^1H and ^{13}C NMR studies.

439. Analysis of Water Samples for Nitrate Ion

Tyler G. Schroeder, student and Sarah J Rossiter, Department of Chemistry, Bowling Green State University, Bowling Green, OH

Analysis of Natural Water Samples for Nitrate

In a recent study, samples of natural water from three locations were acquired and the concentration of Nitrate ion in each was determined. The purpose of this study is to determine whether the pollution created by industrial and agricultural activities causes the nitrate concentration in the water to increase. The first of the three samples was taken directly from Lake Erie in Bay Village, Ohio, which is located near Cleveland and the last two samples were gathered from the Maumee River, a tributary to Lake Erie. One of the river-derived samples was taken near Bowling Green and the other was taken in Grand Rapids, much closer to the point at which the Maumee River flows into Lake Erie. Nitrate content was determined using an ion-selective electrode (ISE). In this testing method, a voltage potential is created which responds to the concentration of a specific ion in solution, in this experiment, that ion being nitrate. The voltage is theoretically logarithmically proportional to nitrate concentration in which QUOTE

. While the results did not behave ideally in respect to the aforementioned equation, a reasonable trend was established.

440. One-Pot Synthesis of 1,1,3,3-Tetramethylguanidine Solvated d-Block Metal Complexes

Christopher B. Durr and Scott D. Bunge, Department of Chemistry, Kent State University, Kent, OH

This project reports the "one-pot" synthesis of several zinc and iron complexes utilizing stochiometric amounts of 2,6- di-tertbutylphenol (H-DBP) and 1,1,3,3-tetramethylguanidine (H-TMG). Each reaction was driven forward by de-protonation of H-DBP and the resultant elimination of volatile hydrocarbons. Crystals of each complex were isolated from solution at -35 ^{o}C. The resultant dinuclear complexes were analyzed using single crystal X-Ray diffraction, elemental analysis, FT-IR, UV-VIS and multi-nuclear NMR.

441. Effects of Free Radical System On Enzyme Activity; Chymotrypsin as a Model Enzyme

Ross VerHeul, Marley Greiner and Robert Wei, Department of Chemistry, Cleveland State University, Cleveland, OH

Oxygen radicals (OR) are known to cause structural and functional changes of a wide range of biological molecules. This study focuses on the relationships between oxygen radicals and proteins. However, there is little direct evidence that free radicals have direct effects on proteins. Here we used chymotrypsin as a model enzyme and xanthine/xanthine oxidase as a system for producing oxygen radicals. We first defined the saturating levels of substrate (xanthine) for the given activity of enzyme to estimate the amount of oxygen radicals produced. Next, we optimized the method for measuring chymotrypsin; there are several published methods, but some of them did not work. We finally decided on a method which uses nitrophenylacetate as a surrogate substrate. This system was optimized and was shown to be inhibited by a known inhibitor TPCK. Using this optimized quantitative system, we plan to test the potential effects of the oxygen radicals on the model enzyme, chymotrypsin.

442. Determination of Mutagenic Polycyclic Aromatic Hydrocarbons by Vibrio Fischeri-Based Assay

Klaire Freeman and Dr.Robert Wei, Department of Chemistry, Cleveland State University, Cleveland, OH

Polycyclic aromatic hydrocarbons (PAHs) are major urban contaminants, many of which have been shown to possess mutagenic properties. Various methods have been used to evaluate potential mutagenic and/or carcinogenic properties of the PAHs in humans, which include DNA strand breakage and comet assay, Ames test, and experiments on rodents. These tests are expensive and/or time consuming. A less expensive alternative is Vibrio fischeri, a bioluminescent marine bacterium commonly used in toxicology tests as part of the `Microtox` system. The goal of this study is to determine if `V. fischeri` is an effective means of differentiating mutagenic and nonmutagenic PAHs. Six PAH concentrations ranging from 0.1 ppm to 5 ppm were used. To determine their relative toxicity, `V. fischeri` were cultured in a complex growth medium. 1 mL aliquots of these cultures were then exposed to 0.5 mL PAH solution at pH 7.0. Inhibition of luminescence was then studied both short and long term.

443. Analysis of Water From the Capital University Primmer Property for NO_3^- ,PO_4^{3-} , and Bacteria: A REEL Undergraduate Laboratory

Michael J. Burgess, Brian E. Huff, David W. Pickering, Matthew S. White and Jens M. Hemmingsen, Department of Chemistry, Capital University, Columbus, OH

The Capital University Primmer Property, located near Logan, Ohio, is being developed as an outdoor teaching laboratory. Water from five locations on the property was analyzed for nitrate ion (NO_3^-), phosphate ion (PO_4^{3-}), and coliform bacteria to develop a profile of the surface water chemistry for future studies. Water from nearby Lake Logan was used as a control because it has the same amount of precipitation as the Primmer Property but is fed through a series of groundwater sources. The concentration of PO_4^{3-} was measured using a spectrophotometric assay, NO_3^- concentration was determined using an ion selective electrode and a standard addition method, and the coliform analysis was done by using Presumptive, Confirmed, and EMB tests. The results of the PO_4^{3-} analysis showed less than 0.05 ppm of PO_4^{3-} in the springs, Hocking River, and Lake Logan. However, PO_4^{3-} concentration measured 0.25 ppm in the outlet of the wetlands and the confluence of the springs. Nitrate ion analysis revealed variation in amounts of NO_3^- ranging from 0.426 to 72.824 ppm. There was no correlation when comparing the NO_3^- levels, PO_4^{3-} levels and bacteria concentration.

This project was performed in the general laboratory at Capital University as part of the Research to Enhance Learning (REEL) consortium. Three weeks were devoted to quantitative analysis of ions and bacterial testing.

444. Progress In Synthesis and Characterization of 4-Acetylamino-2, 7- Di-Tert-Butyl-9-(2,2,2-Triphenylethylidene)- Fluorene

Stacy R. Meeks, Tiffany R. Furbee and Daniel J. Phillips, Department of Chemistry, Bethany College, Bethany, WV

The progress in the synthesis of (E and Z) 4-Acetlyamino-2,7-di-`t`-butyl-9-(2,2,2-triphenylethylidene)-flourene is reported. The target molecule is of interest because the compound has the potential to be a model for a future molecular motor. This project started from fluorene to which was added two `t`- butyl groups in the 2 and 7 positions. Next, the system has placed a nitro group in the 4 position that is later changed into an amino group. Acetylation was performed on the amino group to make an acetylamino compound. The last step that was completed changed the system from a fluourene to a flourenone via oxidation of the 9 position. This will later be reacted with a bromomethylene Wittig reagent and then a trityl group will be added to finish the project.

445. Progress Toward the Synthesis and Characterization of 4-Cyanomethyl-2,7-Di-t-Butyl-9-(2,2,2 – Triphenylethylidene)-Fluorene

Christopher B. Smurthwaite and Daniel J. Phillips, Department of Chemsitry, Bethany College, Bethany, WV

The 9-(2,2,2 – triphenylethylidene)-fluorene moiety has shown potential to be developed into a molecular motor. The making of model compounds to explore the effect of different groups on the molecule's properties are of high interest. In that pursuit the target molecule (E and Z) 4-Cyanomethyl-2,7-di-t-butyl-9-(2,2,2 – triphenylethylidene)-fluorene is being made. The progress to date and its characterization are presented.

446. Accessibility and Affinity of Biotin Binding Sites of Streptavidin Bound to Gold Nanoparticles

Albert King[1], Hugh H. Richardson[2] and Peter J. Tandler[1], (1)Department of Chemistry, Walsh University, North Canton, OH, (2)Department of Chemistry and Biochemistry, Ohio University, Athens, OH

The high affinity of streptavidin to biotin and the stability of the biotin-streptavidin complex have made it an attractive system to use for bioconjugation. Streptavidin is a tetramer with four equivalent biotin-binding sites in aqueous solutions. Gold nanoparticles coated with streptavidin are commonly used in immunocytochemistry because of the high aqueous dissociation constant (10^{-15} M) and the high specificity and because they can be used to aggregate gold nanoparticles. To suppress aggregation of gold-streptavidin nanoparticles in aqueous solution, PEGylated biotin can be used to stabilize individual nanoparticles. However, the binding affinity of avidin to biotin-PEG conjugates has been shown to be lower and for high molecular weight PEG only one binding site was accessible. An open question is how does the binding of streptavidin to gold nanoparticles effect the accessibility and the affinity of the biotin-binding site?

447. Degradation Strength of An Algal-Bacterial Consortium On Pyrene and Benzo[a]Pyrene

Aleks Jovanovich, Department of Chemistry, Cleveland State University, Cleveland, OH

Bioremeidation has proven itself to be an efficient method for degrading polycyclic aromatic hydrocarbons in contaminated soil. A comparative study of the degradation strengths of an algal-bacterial consortium consisting of the algae strain **Chlorella sorokinian, and the bacteria strain** Pseudomonas migula were performed in this project. Tests will be conducted on the algae and bacteria's ability to degrade pyrene and benzo[a]pyrene, model PAH compounds. Conceneations of the PAHs will be monitored over a 10 day period using HPLC-UV analysis. Complete degradation is expected to be achieved between the 216th hour and the 240th hour. Success of this project could provide a cost effective process to clean dangerous and toxic PAH's from the surrounding environment.

448. Determination of Lead and Mercury Ions in the Sediment of the Cuyahoga River

Alan Rossio, Vitaliy Pysmennyy, Scotty Fulton, Jerry Mundell and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

The purpose of this study is to determine the correlation between the concentration of lead and mercury in the sediment and the concentration of these same elements in fish samples obtained from the Cuyahoga River. The sampling region was in close proximity to industrialized Cleveland.

The sediment and fish samples were collected from five locations along the river. The metals were homogenized and extracted from the samples according to EPA method 1311. The samples were then analyzed for metal ions using inductively coupled plasma (ICP).

449. In Vitro Biodegradation of Three Polycyclic Aromatic Hydrocarbons (PAH) by Root Tissues

Elizabeth Maruschak, Robert Wei and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

Polycyclic aromatic hydrocarbons (PAHs) are the major urban pollutants, some of which are known to have mutagenic and or carcinogenic properties. The PAHs are environmentally persistent as they are chemically stable. On the other hand, they are susceptible to degradation by light and certain catalysts. They have also been shown to be degraded by certain bacteria in soil and taken up by plants, but not much is known about the biodegradation mechanisms. Recent studies have shown

that certain root systems are effective in degrading PAHs and that high concentration of linoleic acid stimulated degradation. Four root systems containing relatively high levels of linoleic acid (red radish, daikon radish, carrot and celery root) were selected to determine degradation rates of three PAHs (pyrene, benzo[a]pyrene, and fluoranthene). The roots were macerated in isotonic buffer and 13 day experiments were conducted. The results from the GC-MS analyses of PAHs and their degradation products will be presented

450. Extracellular Vs Intracellular Degradation of Polychlorinated Biphenyls by Pleurous Ostreatus

Michael Arcuri, Ben Wolfe, Aspasia Sicking, Jerry Mundell and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

It has previously been shown that the oyster mushroom, `Pleurotus ostreatus`, a white rot fungus, is capable of degrading polychlorinated biphenyls(PCBs); however it has not been determined whether the initiation of the mechanism occurs intracellularly or extracellularly. After culturing P. ostreatus for a period of three weeks, the fungi’s digestive enzymes (which are excreted into the growth medium through a glass borosilicate filter) will be purified and concentrated through fractionation with an aqueous buffer and ammonium sulfate. The purified protein will then be contaminated with three very different congeners of PCB to determine if the fungi’s excreted digestive enzymes are capable of initiating degradation. Gas Chromatography and Mass Spectrometry will be used to identify and determine recovery percentage of the PCBs.

451. Phytoremediation Removal of Chromium VI From Soil Samples Using Triticum Aestivum and Sorghastrum Nutans

Sandra Vilevac, Juan Carlos Gamarra and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

Chromium (VI), classified as a carcinogen by the EPA, is abundant in Cleveland due to the presence of a steel industry in the downtown area of Cleveland. The removal of Chromium (VI) by phytoremidation from soil was studied. Wheatgrass (`Triticum aestivum)` and Indian Grass `(Sorghastrum nutans)` grown in contaminated soil were used. The fibrous roots of the grasses have been shown to be effective in the removal of metal contaminants in the soil. The remaining chromium (VI) was extracted from the soil after a growing period of 10 days and analyzed for using the diphenylcarbizide colorimetric method. Extraction methods were also performed on the plants to determine if Chromium(VI) was present. We hope to show that these types of grasses (native to Cleveland) can be effectively used in the phytoremediation process.

452. Analysis of Polycyclic Aromatic Hydrocarbons in Soils around Smoking Areas On Cleveland State University Campus

Aloysus Lawong, Robert Wei and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

Polycyclic Aromatic Hydrocarbons (PAHs) have been determined to be carcinogenic in humans, cause deleterious and harmful effects in animals, and are a major environmental hazard. PAHs among other hazardous substances are the by-products of incomplete combustion of oil and gas, and other organic substances like tobacco. Soil from the W. 24th street that runs across the centre of Cleveland State University campus was analyzed because of its constant exposure to automobile exhaust, and also being a frequented smoking area. This study used a direct extraction method and GC/MS characterization to analyze for the presence of benzo-[a]-pyrene in concentrations between 0.1 and 2.0 ppm. The results of the GC-MS analysis will be presented.

453. Determination of Polychlorinated Biphenyls (PCBs) From Transformer Oil Found in Soil

Jayme Kacica, Michael Bauer, Jerry Mundell and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

Electrical transformers used in the seventies and part of the eighties were known to be manufactured with polychlorinated biyphenyls (PCBs) in the insulation of the transformers as well as the transformer oil. PCBs are known to cause cancer in lab animals, and are probable carcinogens in humans. PCBs were widely used in transformers because of their high fire resistance as well as their inability to conduct electricity. This was a viable and cheap option when manufacturing transformers. It was later found they had an effect on the environment. High levels of toxicity caused adverse health affects in humans and animals. PCBs are known to have bioaccumulations. Soil samples were taken from an area where an electrical transformer exploded in the mid 80's. GC/MS will be used to determine if PCBs are present in the samples. Results of the GC/MS analysis will be presented.

454. Analysis of Water From Old Man's Cave and Sunday Creek for Chloride and Iron: A REEL Undergraduate Laboratory

Sierra S. Hill, Janet M. Downs and William J. Clark Jr., Department of Chemistry, Capital University, Columbus, OH

Acid mine drainage (AMD) effects can be found in many waterways in the United States. Streams found near mining sites often have exceptionally low pH and increased concentrations of heavy metals. In this project, water samples from Sunday Creek, known to be affected by AMD, were compared to control samples taken from the Upper and Lower Falls of Old Man's Cave. The samples were tested to determine the concentrations of chloride and iron using ion selective electrodes (ISE) and atomic absorption spectroscopy (AA), respectively. The results showed no detectable difference in chloride concentration between the samples. Substantial differences were observed in iron concentrations, however. The fresh water from Old Man's Cave had iron concentrations near detection limits for the method, while the samples from Sunday Creek had significantly higher concentrations. Additionally, the Sunday Creek samples exhibited lower pH values than samples from Old Man's Cave as expected.

This project was performed in the general chemistry laboratory at Capital University as part of the Research Experience to Enhance Learning (REEL) consortium. Three weeks of the course were devoted to quantitative analysis of ions in natural water samples.

455. A Reinvestigation of the Continuous Absorption Spectra of IBr and Icl

Rachael M. Stuck and David A. Dolson, Department of Chemistry, Wright State University, Dayton, OH

Absorption coefficients of ICl and IBr are of interest because they are photolyzed to produce spin-orbit excited (2P½) Cl* and Br* atoms in energy transfer studies. Notable differences exist for the vapor phase ICl absorption coefficients previously reported - possibly related to sample purity. Only a single gas phase investigation of IBr absorption coefficients has been published. In the present work extinction coefficients for halogen (Cl2 and Br2) and interhalogen (ICl and IBr) vapors were determined in the 200 nm – 600 nm spectral range using a diode array spectrophotometer. Great care was used to prepare ICl and IBr from stoichiometric amounts of the elemental halogens. Results will be compared to currently recommended values and recommended absorption coefficients will be presented.

456. Extraction Efficiency and Rate of Detoxification of Polychlorinated Biphenlys in Wheat Straw Medium

Karina Radonich, Nicholos Yurko, Miranda LaBant, Jerry Mundell and Anne O'Connor, Department of Chemistry, Cleveland State University, Cleveland, OH

Polychlorinated biphenyls (PCBs) are synthetic chemical compounds that were produced in the United States between 1929 and 1977 until the federal government banned their production due to public health and wildlife environmental concerns. PCBs are robust compounds that take decades to naturally degrade in the environment. Oyster mushrooms have been used effectively in the process of bioremediation which has been demonstrated to effectively detoxify PCBs. In this project, the effectiveness of the extraction method and the rate of detoxification of the PCBs, in the presence of oyster mushrooms will be determined. Oyster mushrooms have been grown on wheat straw medium contaminated with a known amount of PCB. The Soxhlet extraction method was used to extract the PCBs from the straw medium and the percent recovery and rate of detoxification will be determined by GC/MS.

457. A REEL Undergraduate Laboratory Water Analysis of NO_3^- and PO_4^{3-} Surrounding the Alum Creek Combined Sewer Overflow in Bexley, Ohio

Alicia Tysl, Rachel Yoho, Megan Deeds, Cassady Allen and Jens Hemmingsen, Department of Chemistry, Capital University, Columbus, OH

Surface water surrounding the Alum Creek Combined Sewer Overflow (CSO) in Bexley, Ohio was analyzed for nitrate (NO_3^-) and phosphate (PO_4^{3-}) ions. This study is significant because the City of Columbus plans on spending $2.5 billion to reduce the effect of CSOs in local waterways. Water sample testing using an ion selective electrode and the standard addition method from four locations surrounding the CSO shows an increase in the nitrate and phosphate levels from upstream to downstream. Preliminary analysis for nitrate shows that the concentration upstream from the CSO was 3.9 ppm NO_3^-, and at the last tested location downstream it had risen to 4.6 ppm. The EPA sets a maximum contaminant level of 10 ppm nitrate ion in drinking water, so with an actual overflow, the concentration of nitrate could be hazardous if consumed. Preliminary analysis for phosphate shows a concentration of .162 ppm PO_4^{3-} at the CSO, while the concentration was 0.0285 ppm upstream and 0.00711 ppm downstream. Phosphate levels in natural water are considered dangerous when exceeding 0.1 ppm PO_4^{3-}. The phosphate concentration at the CSO is already above this limit.

This research was performed as part of the general chemistry laboratory Research Experience to Enhance Learning (REEL) program at Capital University. Three weeks of the course were designated for studying ions and performing analyses of natural water samples.

458. Quinone-Capped Molecular Wires as Electrocatalysts to Detect Thiols: Synthesis and Electrochemical Studies

Brian S. Muntean, Kathryn M. Guinta, Jaskiran Kaur, Thomas R. Wendland, Jhindan Mukherjee, Jon R. Kirchhoff and Liyanaaratchige Tillekeratne, Department of Medicinal and Biological Chemistry, College of Pharmacy, University of Toledo, Toledo, OH

Thiols are important biomarkers of disease and physiological function in biological systems. Therefore, sensors capable of detecting thiols at low concentrations have applications in both medicine and industry. We have previously reported thiol detection at nanomolar concentrations using redox active quinones as electrocatalysts. In these electrochemical sensors, the quinone was trapped in a polymer matrix on a glassy carbon electrode. We have since improved the electrode construction by generating self-assembled mono-layers (SAM) of quinone-capped molecular wires on gold electrodes. The design, synthesis, and electrochemical studies of these molecular wires in selective detection of thiols will be discussed.

NSF Undergraduate Education Grants

Sponsor: Fisher Scientific
Organizer: Weslene Tallmadge Gannon University, Erie, PA
Presider: Robert K. Boggess, Ph. D. Radford University, Radford, VA

Session Overview: The session will feature an overview of NSF programs that support undergraduate education, including presentations by a Foundation Program Director and current awardees in the CCLI, NSDL, ATE, and other programs. Following the presentation, there will be a question/answer session.

459. Programs at the National Science Foundation That Support Teaching and Research Involving Undergraduate Students

Bert E. Holmes, Ph.D., Division of Undergraduate Education, National Science Foundation, Arlington, VA

The National Science Foundation (NSF) supports the efforts of faculty to improve the teaching-learning environment and to establish productive research programs with undergraduates. The Division of Undergraduate Education (DUE) has a number of programs (CCLI, STEP, ATE, NSDL, S-STEM, Noyce, etc) that are of interest to chemists involved in undergraduate education and information will be presented about these opportunities. Support for faculty engaged in research involving undergraduate students are generally housed within the Division of the specific disciplines and a brief overview will be given of NSF programs that fund this research (REU, RUI, ROA, MRI, etc.).

460. Empowering Student Learning in the Geologic Sciences with Three Dimensional Interactive Animation and Low Cost Virtual Reality

Laura Marie Leventhal, Ph.D.[1], Dale S. Klopfer, Ph.D.[2], Guy W. Zimmerman, Ph.D.[1] and Charles M. Onasch, Ph.D.[3], (1)Computer Science Department, Bowling Green State University, Bowling Green, OH, (2)Psychology Department, Bowling Green State University, Bowling Green, OH, (3)School of Earth Environment and Society, Bowling Green State University, Bowling Green, OH

Many tasks in science require processing of spatial information. Learners with low spatial skills may be systematically disadvantaged in fields where teaching methods are slanted towards the use of spatial tasks. The primary goal of this project was to develop, explore, and evaluate the usefulness of three-dimensional, interactive animations (3DIA) in college-level geology education. A 3D animation is interactive if it includes both control and manipulation of animation (3DCA and 3DMA). In our work, the animations are used to teach about topographic map profiling, a task that is thought to use spatial skills.

There were two phases to our project: a laboratory study of our 3DIA materials (Study 1), followed by a pilot study using the 3DIA materials in an introductory geology class (Study 2). In Study 1, students saw a 3DIA tutorial followed by a 3DMA training tool and in Study 2, students saw tutorials in one of four interactive 3D conditions, followed by 3DMA training. Findings across both studies are that students are more accurate on less complex problems, if they have higher spatial ability or if they use the 3DMA training tool. In addition, some results suggests that the 3DMA training tool itself may be effective in teaching a strategy to low spatial students; without the tool, the strategy apparently becomes difficult for these students. For students in all science fields, these results are potentially relevant, suggesting that the use of interactive 3D animations can improve performance and learning on tasks that demand processing of spatial information.

461. Using Modeling and Simulation to Engage and Retain Students In STEM Disciplines

Steven I. Gordon, Senior Director, Ohio Supercomputer Center, Columbus, OH

Three community colleges and the Ohio Supercomputer Center are establishing a shared Associates of Science degree program emphasizing computational science. The presentation will provide an overview of the Associate degree program and provides an example modeling and simulation project used for virtual labs focusing on the major curriculum topics. The project-based learning approach is expected to engage and retain students in the STEM fields and prepare them to complete a bachelor's degree in science. The project was made possible through a grant from the National Science Foundation DUE-0703087 as part of the Advanced Technology Education Program.

462. Collaborative for Excellence in Teacher Preparation for Mathematics and Science in Pennsylvania (CETP-PA)

Narayanaswamy Bharathan, Department of Biology, Indiana University of Pennsylvania, Indiana, PA

Science and math teacher preparation programs of the Pennsylvania State System of Higher Education (PASSHE) have been undergoing systemic reform since August 2000 under the aegis of the NSF-supported Collaborative for Excellence in Teacher Preparation in Pennsylvania (CETP-PA). As CETP-PA pursues its original mission of science and math education reform and support to pre-service and in-service teachers, its progress thus far has it poised to reach out to science, technology, engineering and mathematics (STEM) students and professionals who desire to attain their education degree and/or teaching certification. The PASSHE is committed to addressing the critical shortage of science and math teachers and the Robert Noyce scholarships and stipends are an extension of the services provided by and through the Math and Science Centers established in the CETP-PA project. These Centers have in fact become an institutional focus of the 12 CETP-PA universities. The Math and Science Centers offer professional development for pre-service and in-service teachers. 236 schools, including 45 high-need schools, have active relations with CETP Math and Science Centers, ranging from teachers serving on Center teams and participating in professional development to summer academies to formal field placement agreements for in-service teachers. Recruiting and preparing high quality math and science teachers and the importance of investing in a strong STEM teacher workforce continues to make the Noyce Scholarship Program a priority. For more details visit

URL: http://www.iup.edu/page.aspx?id=51923

Project funded by National Science Foundation: Robert Noyce Scholarship Program: # 0531960

463. The ChemCollective: Virtual Labs, Tutors and Scenario Based Learning for Introductory Chemistry

David Yaron[1], Michael Karabinos[1], Gaea Leinhardt[2] and James Greeno[2], (1)Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, (2)Learning Research and Development Center, University of Pittsburgh, Pittsburgh, PA

The goal of the ChemCollective (http://www.chemcollective.org) is to create a collaborative online collection for chemistry education in which authors and users work together to evolve instructional materials that improve learning. Our virtual lab is a flexible Java applet that allows students to design and carry out their own experiments. Over a hundred virtual lab activities are available that help students connect the algebraic manipulations of the traditional introductory course with authentic chemistry. Tools for authoring virtual labs are also available and over a third of our current labs were contributed by the community. Our scenario based learning activities help students connect chemistry to the real world. These include a murder mystery, detection of arsenic in drinking water, and dyes that stain DNA. A set of tutorials is also available covering stoichiometry and chemical equilibrium. The chemical equilibrium tutorials were based on over two years of research on what makes chemical equilibrium so difficult to teach and learn. The tutorials implement a new teaching strategy that our evaluation studies have found to more than double student performance on difficult equilibrium problems.

Small Chemical Business: True Stories of Success

Sponsor: ACS Division of Small Chemical Business SCHB
Organizer: Joseph E. Sabol CHEMICAL CONSULTANTS, Racine, WI
Presider: Joseph E. Sabol CHEMICAL CONSULTANTS, Racine, WI

Session Overview: This symposium will present aspects of starting and running a small chemical business, including advice on planning, starting, financing, operating, maintaining, and growing a small chemical business from entrepreneurs who will present their insight to others wishing to start a business.

464. D&D Consultants: Employee to Entrepreneur

Carol Duane, Founder & President, D&D Consultants of Mentor, Mentor, OH

In planning the start up of D&D Consultants of Mentor, corporate world business development and marketing skills and experience came in handy very early in the process. As I worked on finding resources and information regarding the logistics of launching a business, strategic choices, key to getting off to a good start, were: figuring out which skills had unique value and could be marketable services, what technical services businesses really needed, and would pay for, and who the optimal target audience should be. Lessons learned, resources and tools will be shared.

465. Embarking On Your Adventure in 'Real World' Chemistry

David M. Manuta, Manuta Chemical Consulting, Inc., Waverly, OH

Operating a successful small chemical business is one of the most challenging endeavors that a professional can do. There are many things that the entrepreneur must consider in order to ensure success. I will speak about the planning that goes into a new business. Working with quality accounting and legal professionals is important. Creating a business plan becomes the road map to success. Having sufficient available financing is critical.

Once the business is "off and running", this new adventure is more than just a 40 hour per week job. Marketing the business plus networking in order to identify top-drawer clients and talented personnel are critical to creating a lasting enterprise. Many "dos and don'ts" will be presented. One or more actual assignments will be presented demonstrating our Mission Statement: "The Application of Fundamental Chemical Principles to Solve Problems."

466. Chemistry and Patent Law: How to Protect Yourself

Daniel A. Thomson, Emerson, Thomson & Bennett, Akron, OH

With companies fighting for research dollars and market share in our difficult economy, one area that can help a company weather the current economic downturn is patent law. Patents grant the patent holder the right to exclude anyone else from making, using, or selling the claimed invention within the United States. It is important for companies and inventors to learn how to adequately protect their valuable intellectual property rights.

467. Analyzing Polymeric Composites and Advanced Materials as a Small Lab – A Risky Business or a Nice Niche Market?

Harlan R. Wilk and Michael P. Mallamaci, PolyInsight LLC, Akron, OH

PolyInsight is a small microscopy lab in northeast Ohio serving the polymer industry. Originally envisioned to provide atomic force microscopy (AFM) services to small and medium sized businesses developing new polymer composites, coatings, and blends, the process of starting and growing the company has contained challenges that were not completely anticipated by the two research scientists who started the company. Things that we've learned include realizing that sales and marketing can't be evil, highly technical people aren't always right, and knowing what you don't know is a step in the right direction. Approaches that we used to address some of our technical difficulties and business challenges as well as some future opportunities will be presented.

468. Evolving Insurance Needs for the Small Business

Ronald J. Versic, Ronald T. Dodge Co., Dayton, OH

Planning for a disaster helps considerably in recovering from one. Properly selected, insurance can protect from losses due to more than hurricane damage. In particular, insurance from losses due to tornados, water backup, water damage and earthquakes can be more important. This paper discusses the benefits of business interruption insurance among others. The Ronald T. Dodge company will discuss the evolving purchase of insurance from the early years (1980's) of no insurance to today's insurance for a 16,000 sq. ft manufacturing facility. Insurance coverage for buildings, building contents, machinery, employees and vehicle is discussed.

469. Selling to the Government

Robert W. Fenn, Program Director, Northeast Ohio PTAC, Painesville, OH

Small businesses should not overlook selling their products and services to the government. This presentation will address the following: 1. Why businesses should consider selling to the government? 2. Can my business sell to the government? 3. Should I sell to the government? 4. Is there someone to guide me? 5. How do I get started? Learn the answers to these questions from a representative from the local Procurement Technical Assistance Center PTAC and be prepared to do business with the government.

Chemical Biology & Medicinal Chemistry (1)

Organizer: Gregory Tochtrop Case Western Reserve University, Cleveland, OH
Organizer: Rajesh Viswanathan Case Western Reserve University, Cleveland, OH
Presider: Gregory Tochtrop Case Western Reserve University, Cleveland, OH

Session Overview: This session will span the chemistry biology spectrum, and focus on the design, synthesis, and evaluation of small molecules against biological systems.

470. Chemical Biology of Marine Natural and Non-Natural Products

Craig J. Forsyth, Department of Chemistry, The Ohio State University, Columbus, OH

Many structurally novel marine natural products present a range of opportunities for probing and modulating biological processes associated with human diseases. A major part of our research program continues to be directed towards exploring these opportunities utilized the enabling power of organic synthesis. In addition to augmenting limiting amounts of biologically active compounds via total synthesis, the design, synthesis and utilization of non-natural products inspired by the structures of natural metabolites has allowed unique studies to be performed. These have illuminated unique biological modes and mechanisms of action, definition of essential pharmacophores, discovery of simplified compounds with enhanced pharmacological profiles, and promoted the development of immunogens for broad applications. Highlights of such recent research accomplishments will described.

471. Small Molecule Modulation of Expression in the Inflammatory Response

Gregory Tochtrop, Department of Chemistry, Case Western Reserve University, Cleveland, OH

Our expanding knowledge of the fundamental processes that underlie the multiple stages of carcinogenesis, including inflammation and mutagenesis, presents significant opportunity to develop novel chemopreventive agents. These processes are linked by common molecular pathways that mediate cellular responses to stress and epigenetic events. Many of the intermediates in these pathways are now recognized as having important roles, including signaling molecules such as phosphatidylinositol-3-kinase, components of the Janus kinase (JAK)/signal transducers and activators of transcription (STAT) pathway, and other transcription factors such as Nuclear Factor kB, and Nrf2. Of these, the leucine zipper transcription factor Nrf2 has emerged as a highly relevant target, as agents that induce this key enhancer of phase 2 enzymes effectively reduce oxidative stress and are cytoprotective. This presentation will focus on small molecule modulators of the Nrf2 pathway and how these small molecules modulate the expression of iNOS and COX-2 in addition to other phase 2 genes which is a hallmark of their activity profile.

472. New Sources of Chemical Diversity Inspired by Polyketide Biosynthesis

Richard E. Taylor, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN

Despite the advent of combinatorial chemistry the number of new biological targets that have emerged from the pharmaceutical industry is remarkably small. These deficiencies can in part be attributed to a lack of chemical diversity in the libraries currently being screened by Big Pharma. Our lab is particularly interested in the correlation between unique natural product structures and their corresponding biological activities. Polyketides evolve during the ancestral history of the producing organism through modification in the polyketide synthase (PKS) gene clusters followed by the development or sequestration of post-PKS processing enzymes. The goal of the project is to generate new sources of chemical diversity based upon the modification of polyketide scaffolds and explore their chemotherapeutic potential. Our program seeks to design, synthesize, and biological evaluate structurally unique derivatives of polyketide natural product such as epothilone, apoptolidin, tedanolide, and neopeltolide based upon modifications of their biosynthetic pathway. Current leads created in our lab include 14-subsituted epothilones based upon biosynthetic relevant alterations to the polyketide backbone. These compounds have been shown to possess single digit nanomolar activity against a range of cancer cell lines. More recently, our lab has targeted polyketide analogues based on elimination of post-PKS process steps since these “shunt” metabolites were likely produced during the evolutionary history of the producing organism. In addition to their unique structure and potentially valuable biological activity, compounds based on modifications to biosynthetic pathways, may be available through fermentation of genetic engineered heterologous organisms thus alleviating the need for large-scale synthetic production.

473. Allosteric Control Over Hsp70 Reveals Its Roles in Neurodegenerative Disease

Jason E. Gestwicki, Department of Pathology and the Life Sciences Institute, University of Michigan, Ann Arbor, MI

Neurodegenerative disorders, such as Alzheimer’s and Huntington’s diseases, are associated with the deposition and accumulation of misfolded polypeptides. The molecular chaperone, heat shock protein 70 (Hsp70), is thought to play important roles in neurodegenerative disease through its ability to regulate the degradation of misfolding-prone proteins. We recently developed a high throughput chemical screen for Hsp70 and identified molecules that permit pharmacological control over Hsp70 function. These compounds bind to Hsp70 at important allosteric sites and “tune” its chaperone profile. Using these probes, we are exploring the relationships between Hsp70 and protein misfolding in models of neurodegeneration.

Computational Chemistry (5)

Organizer: Jane S. Murray, Ph. D. Chemist Cleveland State Universitiy, Cleveland, OH
Organizer: Peter Politzer, Ph. D. Chemist Cleveland State Universitiy, Cleveland, OH
Presider: Peter Politzer, Ph. D. Chemist Cleveland State Universitiy, Cleveland, OH
Presider: Jane S. Murray, Ph. D. Chemist Cleveland State Universitiy, Cleveland, OH

Session Overview: Acknowledgements: We greatly appreciate the support provided by the U. S. Office of Naval Research and the Computers in Chemistry Division of the American Chemical Society.

474. Radiation-Free Actinide Chemistry: Exploring New Bonding Motifs

Jason L. Sonnenberg, Jia Zhou and H. Bernhard Schlegel, Department of Chemistry, Wayne State University, Detroit, MI

The discovery of $Zn(I)_2(\eta^5\text{-}C_5Me_5)^2$ has fundamentally changed the definition of metallocene by introducing dimetallic units to the middle of the classic sandwich complex. Since actinide metallocenes employing COT (COT = $[C_8H_8]^{2-}$) rings are well known, it occurred to us that actinoid dimers may be stabilized by the new dimetallocene bonding motif. Scalar-relativistic density functional theory calculations were employed to investigate the isomers of $[An(n)_2(COT)_2]^{2n-4}$ where n = 2 or 3.

475. Mapping the Network Topology of Chemical Spaces

N. Sukumar, Department of Chemistry and Center for Biotechnology, Rensselaer Polytechnic Institute, Troy, NY and Michael Krein, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY

A network graph can be defined for any chemical space by connecting similar molecules (nodes of the network) by edges. Through analysis of large molecular databases (such as PubChem and ZINC) in terms of atom type environment similarity and similarity of electronic property distributions, network topology and degree distribution are constructed for chemical spaces. This network topology is being employed to address questions such as:

- Do different chemical subspaces possess different topology?
- Can these characteristics be used to refine compound libraries for specific applications?
- When can QSAR models constructed within a given chemical subspace be expected to be robust to random deletion of a significant fraction of training molecules?
- How sensitive is the dependence of network characteristics on the similarity measures employed for construction of the network?

The answers to these questions have obvious implications for the design of high throughput screening libraries.

476. Agent-Based Models for Chemistry and Physics

Paul G. Seybold, Department of Chemistry, Wright State University, Dayton, OH

A brief overview of the use of agent-based models for the simulation of the behaviors of complex systems will be given. It will be emphasized that these agent-based models are rule-based, rather than equation-based, and the models themselves are discrete in state, time, and space. Although the governing rules themselves may be quite simple, quite complex features can emerge from the simulations. Illustrations using stochastic cellular automata models of a phase separation, a chemical reaction, and the vapor-liquid phase transition will be presented.

477. Decision Trees Instead of Linear Regression for Predicting Physicochemical Properties From Chemical Structure

Adam C. Lee and Gordon M. Crippen, Department of Medicinal Chemistry, University of Michigan, Ann Arbor, MI

Traditionally, quantitative structure-activity relations (QSAR) have been formulated as a linear combination of chemical compound properties that should fit the observed activity. Properties may be quantitative, such as logP, or qualitative, such as an indicator variable for the presence of a particular substituent. The advantages are that least squares fitting by linear regression almost always reaches a unique solution for even large problems, and the statistics of the matter is well understood, with standard tests for goodness of fit, predictive power, and overfitting. The disadvantage is that a linear function of purely chemical structural indicator variables may not fit some quantitative observed property very well. Here we show how binary decision trees can readily handle this sort of problem. We have developed a systematic way of constructing such trees for a given training set, where each branch corresponds to the presence or absence of some detailed or rather general feature of the covalent chemical structure. Furthermore, we have established measures of goodness of fit and tests for predictive power, so as to avoid overfitting. Applications of this approach so far include models for cytotoxicity in cell-based assays and for the pKa of monoprotic small molecules. We are currently working to adapt this methodology in order to predict other properties, such as aqueous solubility, boiling point, etc.

Organic Chemistry (2)

Organizer: Steven J. Sucheck University of Toledo, Toledo, OH
Presider: Michael W. Justik Penn State Erie, The Behrend College, Erie, PA

478. Oxidations Using 4-Acetylamino-2,2,6,6-Tetramethylpiperidine-1-Oxoammonium Tetrafluoroborate In Aqueous Media

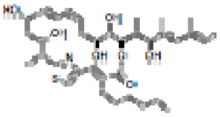
Matthew R. Luderer, Department of Natural Science, Mathematics, and Engineering, University of Pittsburgh at Greensburg, Greensburg, PA

The water soluble oxidant, 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate, has been found to oxidize a variety of aliphatic and aromatic primary and secondary alcohols to their corresponding aldehydes and ketones with and without catalyst in aqueous media in good to excellent yields. The oxidant has also been found to cleave benzyl ethers, oxidize heteroaromatic alcohols, couple primary alcohols containing a beta oxygen, and oxidize epoxides to alpha-hydroxy ketones in aqueous media.

479. Targeting the Total Synthesis of the Anti-Tuberculosis Agents Thuggacins

Ting Wang and Craig Forsyth, Department of Chemistry, The Ohio State University, Columbus, OH

The thuggacins are structurally novel natural products that embody a combination of synthetically challenging structural features and promising anti-tuberculosis activity. These natural products were isolated recently from myxobacterium `Sorangium cellulosum` by Rolf Jansen and co-workers and feature macrolide, thaizole, and a stereochemically dense monoacylated tetraol moiety. Thuggacins A-C are structural variants that differ in macrolide size via variable lactonizaiton among the polyol motif. The OSU approach to the total synthesis of the thuggacins involves the development and application of asymmetric `N`–heterocylic carbene catalyzed acylation to establish the syn stereochemical relationship of the alpha and beta methyl and hydroxyl substituents pendant on the thiazole moiety. Progress towards the total syntheses of members of this novel class of compounds will be summarized.



Thuggacin C

480. Synthesis and Properties of 1,1,2,2-Tetra(3,5-dibromophenyl)-1,2-Ethanediol

Young J. Cho, Department of Chemistry, Central Michigan University, Mount Pleasant, MI and Bob A. Howell, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI

Highly-functionalized 1,2-diols are precursors to strained five-membered siloles which can function as radical initiators for preparation of oligomers and polymers. If the siloles substituents contain aromatic bromine the resultant polymers contain a flame-retarding moiety in the mainchain. An attractive precursor to useful siloles of this kind is 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol. This compounds may be synthesized starting form 1,3,5-tribromobenzene, Lithium-halogen exchange using butyllithium generates 3,5-dibromophenyllithium which may be condensed with ethyl formate to provide di(3,5-dibromophenyl)methanol. Mild oxidation of this alcohol affords di(3,5-dibromophenyl)methanone. Zinc-promoted reductive coupling of the ketone generates the desired diol. The diol, as well as all intermediate compounds, have been fully characterized spectroscopically.

481. Development and Synthesis of Corannulene-Based Organic Materials

Derek Jones and James Mack, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Since their discovery, fullerenes and nanotubes have spearheaded the development of nanotechnology. However, they are difficult to synthesize and modify for specific tasks. Corannulene, which is 1/3 of fullerene [60], has unique fluorescent and electrochromic properties--the process of reversible color change by electrochemical means. Furthermore, corannulene-based organic materials have the potential to advance organic light emitting diode (OLED) technology. Our studies have shown a significant red shift in the absorbance spectra and increased luminescence of the corannulene-based molecules. Also, our studies have shown the ability for a molecule to absorb different wavelengths of light and have the ability to fluoresce multiple colors. Further studies of these corannulene-based materials will help increase the knowledge and allow for applications in nanotechnological fields.

482. Novel Synthesis of Isoxazolo[2,3-α]Pyridinium Salts From Pyridine N-Oxides

Michael W. Justik, Assistant Professor of Chemistry and Samantha L. Kristufek, School of Science, Penn State Erie, The Behrend College, Erie, PA

In previous investigations 'soft' nucleophiles such as arene oxides, arene thiolates and even nitrile N-oxides have been observed to attack alkynyl iodinium salts in a Michael-type reaction to generate alkylidine carbene intermediates which subsequently undergo a 1,5-intramolecular C-H insertion reaction to afford a heterocyclic product (e.g. a benzofuran from the attack of a arene oxide). In the presented research various 1H-1-(1-alkynyl)-1,2,3-benziodoxathiole 3,3-dioxide salts were prepared and subsequently treated with a novel 'soft' nucleophile in the form of substituted pyridine N-oxides at -20 °C in dichloromethane solvent. The products of these reactions were determined to be isoxazolo[2,3-ɑ]pyridinium salts, heterocycles which contain cationic nitrogen bridging two aromatic rings. The effects of substitution both within the alkynyl iodonium salt moiety as well as on the pyridine *N*-oxide ring were also studied. Previous research has determined that aryl substituted isoxazolo(2,3-ɑ)pyridinyl halides are useful as anti-inflammatory agents and that these compounds are substructures of promising pharmaceuticals for the treatment of cancer, arthritis, inflammation, and other disorders.

483. Corannulene Based Organic Materials

Praveen Bachawala and James Mack, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Palladium catalyzed Sonogashira coupling reactions are used to further extend the aromatic framework of corannulene-a polyaromatic hydrocarbon. Novel derivatives obtained are further examined for their photophysical process and their role in synthesizing blue fluorescent materials.

Organic Chemistry: Nucleic Acids, Peptides, and Glycans (2)

Sponsor: ACS Division of Organic Chemistry, Quanta BioDesign, Ltd., Toledo Section of the ACS
Organizer: Xue-long Sun Cleveland State University, Cleveland, OH
Organizer: Steven J. Sucheck The University of Toledo, Toledo, OH
Presider: Jun J. Hu University of Akron, Akron, OH
Presider: Steven J. Sucheck University of Toledo, Toledo, OH

484. Oriented Immobilization of Glyco-Capturing Macroligand and Its Glyco-Proteomics and Glycomics Application

Xue-long Sun, Chemistry, Cleveland State University, Cleveland, OH

Functional investigation of biomolecules typically starts by reducing the sample complexity through multidimensional separation methods based on the unique characteristics of the biomolecules followed by identification. We report here a chain-end functionalized glycopolymer and boronic acid-containing polymer (boropolymer) as oriented multivalent glyco-affinity capture ligands for efficient purification and identification of carbohydrates-binding proteins and carbohydrate-containing proteins. Briefly, biotin chain-end glycopolymer and boropolymer were synthesized via a biotin derivatived arylamine initiated cyanoxyl-mediated free-radical polymerization in one-pot fashion. Oriented and covalent immobilization of chain-end functionalized glycopolymer and boropolymer onto solid surfaces, such as magnetic beads, mica, and glass slide were investigated and confirmed by fluorescent imaging and AFM techniques. In addition, glyco-affinity capturing and glyco-capture were demonstrated by using magnetic bead founctionalized with the biotin glycopolymer and boropolymer followed by direct MALDI mass spectrometry identification.

485. Factors Governing Protein-Glycan Specificities

Suri Iyer, Dan M. Lewallen and David Siler, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Several toxins and pathogens use cell surface glycans that decorate the surface of eukaryotic cells to gain cell entry. Using chemically defined glycans, we demonstrate that binding between the glycan and its cognate receptor is dependent on glycan structure, density, topology and assay conditions. Specifically, we will present our most recent results on the binding of influenza hemagluttinin and sialic acids.

486. Synthesis of Functionalized Carbohydrates and Their Conjugates

Steven J. Sucheck, Department of Chemistry, MS602, University of Toledo, Toledo, OH

Carbohydrates are ubiquitous substances in nature and represent the most abundant of the major classes of biomolecules. Their diverse structures are typically found in polymeric form, attached to proteins and lipids, or in the form of small molecule glycosides. Saccharides are often identified as structural elements or recognition markers in biological systems and frequently, glycosylation profiles can be diagnostic of disease states such as in cancer. To understand the various roles of carbohydrates and exploit their medicinal potential, we have begun to investigate new approaches to the synthesis of glycopeptides and glycoconjugates using novel ligation reactions. Thusfar, targets have been related to the tumor-associated carbohydrate antigens of MUC1. In addition we have explored modification of carbohydrates and their use as potential inhibitors of enzymes that use carbohydrates as substrates. In particular, we are examining the antigen 85 complex, a homologous family of acyltransferases, which act on the arabinogalactan of `Mycobacterium tuberculosis`.

487. Thermally-Induced Dielectric Relaxation Spectra of Aldohexose Monosaccharides

Alan Riga, PhD[1], Libby N. Kellat[1], Michael Ellen Matthews, BA, MPA[1] and Xue-long Sun[2], (1)Department of Chemistry, Cleveland State University, Cleveland, OH, (2)Chemistry, Cleveland State University, Cleveland, OH

D-Mannose and D-Galactose are C-2 and C-4 epimers of D-Glucose. These aldohexoses are the most common in biological systems and nature. This carbohydrate research is prompted by the previous observation of dielectric loss spectra and excimer formation in amino acids (i.e. L-Arginine and L-Histidine), drugs (i.e. sulfapyradine and tolbutamide), as well as chemicals like anthracene (known to form a dimer/excimer in the solid state) and naphthalene.

Three aldohexose monosaccharides, D-Glucose, D-Mannose and D-Galactose, were examined by scanning temperature Dielectric Analysis (DEA) from ambient temperatures through their melts. Phase transitions, including glass transition (Tg) and melting temperature (Tm), were evaluated by Differential Scanning Calorimetry (DSC). The second and third DEA curves of each aldohexoses were characteristic of an amorphous phase, with highly enhanced conductivity (DEA) and a definitive second run Tg (DSC).

The monosaccharides were found to exhibit thermally-induced dielectric loss spectra or Dielectric Visco-elastic properties in their solid state prior to melting. Activation energies for electrical charging of each of the monosaccharides were calculated from an Arhennius plot of peak frequency versus reciprocal temperature. The DEA profiles were also correlated with the DSC phase diagrams, showing the changes in electrical behavior associated with solid-solid (excimer formation) and solid-liquid (melting) transitions.

488. Glycan Encapsulated Gold Nanoparticles Inhibit Shiga Toxins

Ashish A. Kulkarni and Suri S. Iyer, Department Of Chemistry, University of Cincinnati, Cincinnati, OH

Shiga toxins, released by `Escherichia coli O157:H7` and `Shigella dysentriae` have been implicated as major causes of lethal, food-borne illness that typically affects immunocompromised population. Shiga toxins belong to the AB_5 family of toxins. The homo-pentamer B- or binding subunit binds to the carbohydrate receptor Gb3, and delivers A- subunit to its cycloplasmatic target. The two main serotypes, Shiga toxins 1 and 2 (Stx1 and Stx2) are the major virulence factors, of which Stx2 has been shown to be 500 times more potent than Stx1 in mouse, murine models and epidemiological studies. Vaccines are not available and treatment is mainly passive as antibiotic administration after infection kills the pathogens but increases toxin production. Therefore, there is a great need for the development of therapeutics against Shiga toxin.

We have developed glyconanoparticles as potential anti-adhesion agents. These glyconanoparticles are highly soluble, stable under variety of conditions, non-toxic and could therefore be used as potential therapeutics. Our preliminary studies suggest that glyconanoparticles inhibit toxins from killing Vero cells. We have also demonstrated that toxin inhibition is highly dependent on the structure of the glycan and glycan density. We will present these results.

489. Combinatorial Chemistry: From Cell Signaling to Catalyst Development

Dehua Pei, Department of Chemistry, The Ohio State University, Columbus, OH

A high-throughput method has been developed to synthesize, screen, and decode combinatorial peptide libraries (both linear and cyclic). This method has been applied to determine the peptide motifs recognized by proteins and the optimal substrates of enzymes. The consensus motifs are then used to search the protein databases for the potential protein targets of the modular domains/enzymes. The candidate proteins are subsequently validated (or rejected) by conventional cell biology techniques. This presentation will describe the application of this method to the identification of the partner proteins of several types of protein modular domains (e.g., SH2 and PDZ) and the protein substrates of protein tyrosine phosphatases. The identification of cyclic peptides as inhibitors of protein-protein interaction and organocatalysts will also be discussed.

Physical Chemistry (3)

Organizer: Carlos E. Crespo-Hernández Case Western Reserve University, Cleveland, OH
Organizer: Sarah J. Schmidtke College of Wooster, Wooster, OH
Presider: Sarah J. Schmidtke College of Wooster, Wooster, OH
Presider: Carlos E. Crespo-Hernández Case Western Reserve University, Cleveland, OH

490. Solvation and Dynamics in Ionic Liquids

Sergei Arzhantsev, Hui Jin, Xiang Li and **Mark Maroncelli**, Department of Chemistry, The Pennsylvania State University, University Park, PA

Ionic liquids (ILs) are molten salts made from sufficiently large and asymmetrically shaped cations and anions that these substances are liquid at or near room temperature. This relatively new class of materials is currently being explored for a variety of purposes, including green(er) replacements for conventional organic solvents. We have been using electronic spectroscopy to explore the nature of solvation and simple chemical reactions in ionic liquids. Our work, and that of many other groups, has shown that equilibrium solvation in ILs is often surprisingly similar to that found in highly dipolar organic solvents. Dynamically, however, ILs are distinctive. In contrast to the situation in conventional room-temperature solvents where solute-solvent interactions usually relax on a 1-10 ps time scale, complete relaxation in ionic liquids typically requires several nanoseconds. The solvation response in these liquids is broadly distributed in time, extending from the 100 fs range out to tens of nanoseconds. This slow and broadly distributed solvation response has a pronounced retarding effect on solvent-controlled processes and it gives rise to heterogeneous kinetics for chemical reactions and other processes that occur on picosecond and nanosecond time scales. Heterogeneity is manifest in both non-exponential and excitation-wavelength dependent kinetics of excited-state reactions. I will provide an overview of what is currently known about solvation and kinetics in ionic liquids and present some of our most recent results in this area.

491. Effects of Aggregation On the Properties of Individual Conjugated Oligomers and Polymers Probed by Fluorescence Microscopy and Stark Spectroscopy

Gizelle A. Sherwood, Ph. D. [1], **Linda Peteanu**[1], Alberto Moscatelli[1] and Jurjen Wildeman, Ph. D. [2], (1)Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, (2)Department of Polymer Chemistry and Materials Science Centre, University of Gröningen, Gröningen, Netherlands

The recent upsurge in use of conjugated polymers in photovoltaic devices and in displays drives the need for understanding how morphology affects important functional features such as emission and charge migration. Due to the inherent complexity of polymers, a parallel effort to 'build-up' understanding of their features `via` a detailed study of important electronic and photo-physical properties of oligomer aggregates is needed. These exhibit remarkably uniform spectral properties that defy analysis via standard exciton coupling models. Fluorescence microscopy is used to probe both variations in vibronic structure and emission lifetime between individual aggregates and trends in these properties as a function of aggregate size. Stark spectroscopy, or the measurement of the perturbation of the absorption or emission spectrum with applied electric field, is used to infer the effect of aggregation on the electronic delocalization and charge-transfer properties of these systems.

492. Tracking Ultrafast Equilibrium and Nonequilibrium Chemical Reactions with Multidimensional Infrared Spectroscopy

Jessica M. Anna, Carlos R. Baiz, Robert McCanne, Matthew J. Nee and **Kevin J. Kubarych**, Department of Chemistry, University of Michigan, Ann Arbor, MI

Ultrafast chemical reaction dynamics can be tracked in real time using structurally-specific multidimensional infrared spectroscopy. This talk will present our recent progress in both equilibrium and non-equilibrium chemical transformations in several metal carbonyl complexes. In dicobalt octacarbonyl, we have directly observed equilibrium chemical exchange on the picosecond time scale between two distinct structural isomers. In dimanganese decacarbonyl we have used transient, non-equilibrium 2DIR to watch the slowing of orientational relaxation of the nascent manganese pentacarbonyl photoproduct as it cools. In the cyclopentadienyl molybdenum tricarbonyl dimer, we have used transient 2DIR to observe directly the non-equilibrium geminate rebinding process. Finally we present results on equilibrium and non-equilibrium investigations of the cyclopentadienyl iron dicarbonyl dimer and the ruthenium analogue. Metal complexes are central to homogeneous catalysis and artificial light harvesting strategies, and the structural and spectral resolving power of 2DIR spectroscopy offers a sub-picosecond probe of this rich chemical reactivity.

493. Solvent Effects in the Vibrational Cooling Dynamics of 1-Nitronaphthalene in the Triplet Manifold

Christian Reichardt, R. Aaron Vogt and Carlos E. Crespo-Hernández, Department of Chemistry, Case Western Reserve University, Cleveland, OH

The electronic energy relaxation of 1-nitronaphthalene (1NN) was studied in various solvents using broadband transient absorption spectroscopy with femtosecond time resolution. UV excitation of 1NN populates the unrelaxed $S_1(\pi\pi^*)$ state, which decays by conformational relaxation (primarily twisting of the NO_2 group) with a time constant of ~100 fs. The twisting of the NO_2 group and formation of a structurally relaxed singlet state opens up a doorway for ultrafast intersystem crossing to a high-energy receiver triplet state $T_n(\pi\pi^*)$. The receiver T_n state then undergoes ultrafast internal conversion to form the vibrationally excited $T_1(\pi\pi^*)$ state. In protic solvents, vibrational cooling effectively competes with solvent reorientation in the triplet manifold of 1NN. According to this kinetic model, which was first proposed by our group to explain the excited-state dynamics of 1-nitropyrene, the S_1 electronic energy decays rapidly and irreversibly to dark triplet states, explaining why small nitro-polycyclic aromatic compounds are typically considered to be nonfluorescent. Our results are at variance with those presented recently by others. This work was supported by a grant from the American Chemical Society Petroleum Research Fund, Type DNI.

494. The Photochemistry of Small Polyatomic Molecules in Solution

Patrick Z. El-Khoury, Mr., Chemistry, Bowling Green State University, Bowling Green, OH and Alexander N. Tarnovsky, Department of Chemistry and The Center for Photochemical Science, Bowling Green State University, Bowling Green, OH

Abstract. Our recent work focuses on ultrafast photoinduced processes in condensed phases, which we probe using femtosecond time-resolved transient absorption spectroscopy in concert with ab initio CASSF calculations. Novel experimental pump-probe results will be presented on the simultaneous three-body 266-nm photodissociation of CF_2I_2 in solution. The ultrafast excited state relaxation of CF_2I_2 upon 350 nm excitation will be compared. In addition, novel pump-probe data and CASSF results on ultrafast photochemistry of CH_2I_2 in several organic solvents will be presented. New light on the interpretation of 100-ps time-resolved x-ray diffraction experiments on solvated (methanol) CHI_3 will be shed using the acquired pump-probe spectra.

Chemical Education: College Level

Sponsor: Fisher Scientific
Organizer: Weslene Tallmadge Gannon University, Erie, PA
Organizer: Sherri Lovelace-Cameron Youngstown State University, Youngstown, OH
Presider: Weslene Tallmadge, Ph. D. Gannon University, Erie, PA
Presider: Sherri Lovelace-Cameron, Ph.D. Youngstown State University, Youngstown, OH

Session Overview: The purpose of the session is to describe improvements to college level chemistry courses, programs, labs or curricula. Presentations will focus on specific changes and assessment of those changes.

495. Should General Chemistry Read Journal Articles? Student Perspectives On the Inclusion of Primary Literature in Science Courses

Ted M. Clark, Department of Chemistry, the Ohio State University, Columbus, OH

The role of Peer-Mentors in the Research Experiences to Enhance Learning (REEL) program is complex since these students may be viewed as both teachers and students, and as both novice and experienced researchers. Peer-Mentors are situated to provide insights into novel or atypical laboratory tasks included in the General Chemistry curriculum. In this presentation, Peer-Mentor perspectives on assignments designed to introduce undergraduates to primary literature that support authentic classroom-based research will be discussed. Several themes will be considered, including student insights into the Nature of Science and the internet as a resource supporting student access to primary literature.

496. Inclusion of Technology Into a General Chemistry Course

Erica L. DiCara, Ph.D., Department of Chemistry, Gannon University, Erie, PA

Students new to chemistry or who have only taken high school chemistry may not fully come to a necessary understanding of the subject during college instruction. This, I feel, is largely due to the fact that chemistry asks students to understand naturally occurring events that they can not see; events and processes that take place at the molecular and atomic levels. My goal is to use more creative and innovative technological resources to aid in the students' understanding of chemistry. Pre- and post-assessments were given using ANGEL Assessment tool to determine knowledge of chemistry before the course began and retention at the conclusion of the course. This information aids in understanding the chemistry background of students and how well they retain introductory topics at the end of a semester of chemistry.   Using this information, I can fine-tune my lectures to enhance the learning experience. A discussion board covering a current event in science was held using ANGEL Discussion Forum tool. This discussion board aided in allowing students a glimpse into the social relevance of science. A video of the topic was presented in class, and the students were required to do more research and post their thoughts.

497. The Kitchen Is Your Laboratory: A Useful Method for a Research-Based Term Paper Assignment In a Scientific Writing Lecture Course

Clinton D. Jones, Department of Chemistry and Biochemistry, Mercyhurst College, Erie, PA

An undergraduate level course dedicated to scientific writing and communication is extremely useful for all science majors, as it can provide a tangible link between their gained fundamental knowledge and becoming a peer in the scientific community. Such courses do not often include a laboratory component. However, in my ideal pedagogical approach to a scientific writing course, students would collect empirical data and compose a research manuscript as a term paper. I have overcome the lack of a laboratory component in such a course by asking students to develop their own experiments and collect their own data from their personal laboratory – their kitchens. Motivating students to use food preparation as a chemical experiment does more than just provide them with adequate data for their term papers. Students develop a new awareness for chemical and physical variables, acquire experimental planning and development expertise, and most seem to gain an enhanced set of independent thinking skills. The assignment requires students to treat every ingredient in the meal as a chemical and each piece of kitchen equipment as scientific instrumentation. Students are required to provide correctly formatted scientific terms for consumables and equipment; they are also encouraged to bring their experimental results into the classroom for statistical taste-test data. Each work culminates with the submission of a communication-type manuscript properly formatted by using the Journal of the American Chemical Society's Communication Template. The details of this assignment are presented along with resulting sample term papers from students over the past two years.

498. Students Teaching Students: The Training of Peer-Mentors in Chemistry

Ted M. Clark, Department of Chemistry, the Ohio State University, Columbus, OH

The Research Experiences to Enhance Learning (REEL) program, as implemented in General Chemistry at the Ohio State University, uses Peer-Mentors to support approximately 700 undergraduate students in classroom based research. Peer-Mentors are undergraduates that have completed a REEL research module and return to support the research of other undergraduates. In this presentation, issues surrounding Peer-Mentors recruitment, training, and utilization will be discussed. The preparation of Peer-Mentors is crucial for the successful implementation of REEL at OSU, but also a work in progress and novel challenges and opportunities exist when training these students. The perspective of Peer-Mentors and their assessment of training and preparation will be shared.

499. The Development of a Research-Based Laboratory Module for the Undergraduate Organic Chemistry Laboratory

Steven J. Sucheck, Department of Chemistry, MS602, University of Toledo, Toledo, OH and **Treasure J. Sucheck**, Department of Chemistry, Mercy College, Toledo, OH

A dynamic, 4-week, research-based module for the undergraduate organic chemistry lab was developed as part of the NSF sponsored Ohio REEL-Research Experiences to Enhance Learning project. The research module is centered on the synthesis of N-aryloxazolidinones, an important organic pharmacore which possesses a variety of biological activities. The synthesis of the oxazolidinone based compounds involves a blend of traditional organic chemistry with newer techniques such as parallel synthesis and microwave synthesis. The resulting library of compounds are screened against several organisms for antibiotic activity. The initial set of laboratory modules were developed and incorporated into the organic chemistry lab curriculum at The University of Toledo. Adaptations of the lab module are currently being beta-tested in an organic chemistry lab course at Mercy College. This collaboration represents the beginning of a local network of educators from diverse institutions who can share expertise as they implement new research based laboratory modules and conduct undergraduate research.

500. Experiential Learning for a Doctor of Pharmacy Student: A Rotation as An Organic Chemistry Faculty Member at a Primarily Undergraduate Institution

Vincent Maloney, Chemistry Department, Indiana U. Purdue U. Fort Wayne, Fort Wayne, IN and Christopher Liston, PharmD Candidate, School of Pharmacy and Pharmaceutical Sciences, Purdue University, West Lafayette, IN

This presentation describes the atypical academic clerkship rotation of a pharmacy student as an organic chemistry faculty member at a primarily undergraduate institution. Doctor of Pharmacy students at Purdue University's School of Pharmacy and Pharmaceutical Sciences complete 44 weeks of clerkship rotations (experiential learning). Normally these rotations are in typical settings such as hospitals and pharmacies. A 4- week academic clerkship rotation involving assignments representative of academic careers is provided at the W. Lafayette campus as an option for those interested in academia. The design and management of this unorthodox academic rotation at Indiana U. Purdue U. Fort Wayne will be described. Not only were there obvious benefits for the pharmacy student and the students taking organic chemistry lecture and lab, but also there were salutary benefits some of which were unexpected for the preceptor of the rotation. This clerkship rotation can serve as model for experiential learning for professional students and graduate students in chemistry.

501. Investigating Drinking Water Quality: Theme-Based Activities for a Range of Instructional Levels

Katherine C. Lanigan and Elizabeth S. Roberts-Kirchhoff, Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, MI

Drinking water quality is the theme for several related projects presented here. College level activities for allied health majors and science majors as well as those adapted for junior high school students are described. The projects involve researching U.S. Environmental Protection Agency guidelines and water quality reports published by municipalities in addition to examining drinking water hardness both by titration and atomic absorption spectroscopy. Assessment of the pedagogical impact of these was determined from students' written commentary, content and attitude surveys, exams, personal interviews, and classroom observations. The projects resulted in an increased awareness of and enthusiasm for environmental issues as well as knowledge of environmental topics and analytical methods by students at various levels of chemistry instruction.

502. Teaching Energy and Environmental Chemistry to Non-Science Majors --- Learning by Doing Approach

Reiko M. Simmons, Ph-D and Jennifer N. Willians, Department of Chemistry, Cleveland State University, Cleveland, OH

Frequently, students make critical decisions without considerations for the fundamental chemical information involved in the issues. Therefore, it is important, particularly for the non-science majors, to have successful experience and learn some basic chemistry principles and methods. To meet the needs of these students with myriad of backgrounds and skills, all out attempts are made to employ many types of well known educational principles. In particular:

- Encourage full participation (give points for participation, use in-class time for working problems, introduce games, & etc.).
- Promote individual interests (considerable section of the grade given to group & individual research and project presentation, frequent reference to societal issues).
- Use multi-sensory approaches (use of computer web, films & etc.).

- Use concrete materials and experiences (demonstrations & experiments).
- Encourage skill practices (use of games, worksheets, & corrections).
- Streamline goals & objectives (use of concept maps, home work problems à exam questions).

All stops are pulled, in other words, to "ENGAGE" the students to realize the importance of chemical information in our lives.

503. Transesterification of Waste Vegetable Oils and Extracts of Coffee Grounds: A Study of Biodiesel Products in An Undergraduate Chemistry Course

Lois Zook-Gerdau and Ray Rataiczak, Department of Chemistry, Muskingum College, New Concord, OH

Chemistry majors in their junior year at Muskingum College are required to take an advanced laboratory course that integrates their accumulated chemistry skills with instrumental analysis techniques. To better prepare our students for their future scientific careers, mini research projects that crossover the major sub-disciplines of chemistry are incorporated into the course. During the Spring 2009 semester an environmentally themed project involving the production and analysis of biodiesel was introduced into the curriculum. Organic chemistry skills were reinforced through the extraction of oils from coffee grounds and the transesterification reaction of these oils (as well as waste vegetable oils) into biodiesel products. Students then used a variety of analytical and physical chemistry techniques to characterize their oils, including High Performance Liquid Chromatography, Gas Chromatography-Mass Spectrometry, Bomb Calorimetry, and UV-Vis Spectroscopy. Student skills emphasized in this project include researching, following, and modifying procedures found in the chemical literature, identification of appropriate experimental strategies using proper controls, qualitative and quantitative analysis of complex mixtures, both independent and team laboratory work, data management and laboratory note-taking skills, and the ability to analyze, interpret, and evaluate (statistically where necessary) data from an experiment to form a conclusion. Both experimental results of the biodiesel project as well as assessment of student learning throughout the completion of the project will be presented.

Energy Storage and Energy Conversion: Space Power

Organizer: Michelle A. Manzo NASA - Glenn Research Center, Cleveland, OH
Presider: Michelle A. Manzo NASA - Glenn Research Center, Cleveland, OH
Presider: Sri R. Narayan Jet Propulsion Laboratory, Pasadena, CA

Session Overview: NASA is actively pursuing the development of advanced electrochemical energy storage and conversion devices for future lunar and Mars missions. The Exploration Technology Development Program, Energy Storage Project is sponsoring the development of advanced Li-ion batteries and PEM fuel cell and regenerative fuel cell systems for the Altair Lunar Lander, Extravehicular Activities (EVA), and rovers and as the primary energy storage system for Lunar Surface Systems. This session highlights some of the ongoing efforts in support the development of safe, human-rated, reliable, lightweight energy storage and conversion systems to meet those mission requirements.

504. High Energy Density Cathodes for Next Generation Lithium Ion Batteries

Arumugam Manthiram, Texas Materials Institute, University of Texas at Austin, Austin, TX

Lithium ion batteries have revolutionized the portable electronics market, but the structural transitions and the chemical instabilities arising from an overlap of the $Co^{3+/4+}$:3d band with the top of the O^{2-}:2p band limit the practical capacity of the currently used layered $LiCoO_2$ cathode to 50 % of its theoretical capacity. Moreover, $LiCoO_2$ suffers from high cost, toxicity, limited power capability, and safety concerns. These difficulties have created enormous interest in the development of alternative cathodes for next generation lithium ion batteries. In this regard, solid solutions between layered $Li[Li_{1/3}Mn_{2/3}]O_2$ and layered $Li[M]O_2$ ($M = Ni_{1-y-z}Mn_yCo_z$) have become appealing as they exhibit two times higher capacity than $LiCoO_2$ while lowering the cost and improving the safety. However, these layered oxide solid solutions exhibit an irreversible loss of oxygen from the lattice during first charge and a huge irreversible capacity loss in the first cycle. This presentation, after first focusing on the factors influencing the discharge capacity and irreversible capacity values, will concentrate on reducing the irreversible capacity loss and increasing the discharge capacity while improving the rate capability. Specifically, surface modification of the layered oxide solid solution cathodes with other oxides like Al_2O_3 and $AlPO_4$ to reduce the irreversible capacity loss and increase the rate capability as well as mixing the layered oxide cathodes with lithium-free insertion hosts like V_2O_5 to eliminate the irreversible capacity loss will be presented. Optimized compositions that exhibit capacities as high as 300 mAh/g with high rate capability will be presented.

505. Ultrafine Mixed Oxide Cathode Material for Advanced Li-Ion Cells

Jinxiang Dai[1], Ganesh Skandan[1], Farid Badway[1], Krista Martin[1] and Ying Meng[2], (1)NEI Corporation, Somerset, NJ, (2)Department of Materials Science and Engineering, University of Florida, Gainesville, FL

High energy density and high power density Li-ion rechargeable batteries that can operate in a wide voltage range are needed for future applications. Today, Li-ion batteries have become the primary choice for portable applications, including cellular phones, laptop computers, GPS, cameras, and power tools. Nonetheless, Li-ion cells need improvements for future applications, such as electric vehicles and aerospace applications. Commercially used Li-ion batteries have a specific energy in the range of 100-150 Wh/kg. It is a major challenge to increase the specific energy and cycle life of Li-ion batteries over a wide voltage range.

The cathode material is one of the major components that limits the energy density and operating voltage range. Currently available commercial cathode materials, such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$, have a practical specific capacity of < 160 mAh/g, and the maximum operating voltage is < 4.4V. A new generation of ultrafine cathode materials are being developed to deliver high capacity (>200mAh/g) in a wide voltage range (2.5-4.5V). The composite materials with the general formula of $xLi_2MnO_3\cdot(1-x)LiMn_{0.5}Ni_{0.5}O_2$ have been synthesized in the form of ultrafine and phase pure powders. These materials are promising for high specific energy and high voltage Li-ion applications. The performance of the cathode material is affected by the structure, composition and morphology, which have been characterized by x-ray diffraction (XRD), elemental analysis, and electronic microsopy. The correlation between cathode material characteristics and its performance in lithium and lithium-ion cells wil be discussed in the presentation.

506. Metal Phosphate Coating for Improved Cathode Material Safety

Christopher M. Lang and Aron Newman, Physical Sciences Inc., Andover, MA

Physical Sciences, Inc. (PSI) has refined a procedure for coating $LiCoO_2$ with a metal phosphate layer for improved safety. The metal phosphate layer offers greater thermal stability than the base metal oxide material and may be applied through common processing steps that can be scaled to coat materials on a production scale. Energy dispersive spectroscopy mapping, elemental analysis, and x-ray diffraction measurements have been utilized to determine the phosphate content. The impact of coating method and phosphate content on the electrochemical performance of the cathode material and its implications for improved safety will be discussed. Differential scanning calorimetry measurements demonstrate improved thermal stability for metal phosphate coated cathode material, and indicates a likelihood for minimizing thermal runaway in battery systems.

507. Physical Properties, Thermal Stability and Flammability of the Electrolyte Solutions for Lithium-Ion Batteries

Boris Ravdel, Yardney Technical Products, Inc., Pawcatuck, CT and Brett L. Lucht, Department of Chemistry, University of Rhode Island, Kingston, RI

YTP and URI have focused the efforts in three major directions:
- Nature, composition, and temperature effects on conductivity and viscosity of the electrolyte solutions for LIB;
- Their thermal stability and flammability;
- Their stability to electrochemical oxidation and reduction.

We will present results of our measurements, as well as qualitative and quantitative analysis of the conductivity and viscosity of various commercially available salts ($LiPF_6$, $LiBF_4$, LiBETI), and salts developed and synthesized at YTP and URI, in blends of organic carbonates and other solvents. The temperature range for the measurements was -40 to 80°C, and the salt concentrations varied from 0.001 to 2 mol/l.

To quantitatively describe the conductivity – temperature curve, we employed the Vogel-Tammann-Fulcher physical model.

Typical electrolyte solutions for LIB degrade at the temperatures above 70°C. We will discuss the mechanism of the solution decomposition, and the ways to diminish it. Based on our model of the degradation, we developed several species that increase thermal stability of the solution. We discovered that many solid electrode materials impede the process due to a surface film formation as well. The results of our studies of the surface films will be also presented.

As to the electrolyte solution flammability, we tested several nitrogen and phosphorus containing species as additives and discovered that some of them have flame-retarding and thermal-stabilizing effects simultaneously.

Recently, YTP began to develop high-voltage (so called, "5-Volt") cathode materials. The electrochemical window expansion requires the development of new electrolyte solutions stable to electrochemical oxidation at high potentials. We will discuss this problem as well.

508. Advanced Product Water Removal (APWR) Fuel Cells for Future Space Missions

William F. Smith, Infinity Fuel Cell and Hydrogen, Inc., Windsor, CT

Management of two-phase fluids in microgravity has been a challenge since the inception of the space program. Fuel cell power plants produce water as a reaction by-product requiring zero-gravity two-phase water management of the product water. The earliest space fuel cells, used by the Gemini and Biosatellite programs were Proton Exchange Membrane (PEM) "non-flow through" systems that removed product water by various passive methods. The Shuttle Orbiter alkaline fuel cell system uses active rotating equipment for separation of water from reactants. PEM based designs have been proposed that require circulation of one or both reactants to remove and manage water. These "flow through" approaches require circulation loops that usually use active rotating equipment leading to decreased reliability. Such equipment, also consumes parasitic power leading to higher mission reactant launch weights.

With the support of the NASA Glenn Research Center, Infinity Fuel Cell and Hydrogen Inc. is developing a proprietary Advanced Product Water Removal (APWR) technology that promises to eliminate the need for active rotating equipment required for circulation of reactants. This APWR technology has a heritage dating back to the original Gemini missions but has been updated to incorporate 21st century materials and manufacturing techniques. It holds the potential to benefit future NASA missions by reducing overall launch mass, increasing system reliability and increasing fuel cell life.

This paper will review the history of water management on NASA fuel cell programs, review potential benefits of non-flow through systems and summarize the development of Infinity's APWR technology to date.

509. Developments in Passive Fuel Cell Performance for Lunar Missions

Katherine E. Ayers, Director of Research and Luke T. Dalton, Proton Energy Systems, Wallingford, CT

NASA has long identified fuel cells and regenerative fuel cells as the most promising, highest energy density solutions to long endurance power generation and energy storage applications. The return to the moon and eventual exploration of Mars will require fuel cells capable of operating with near 100 percent utilization of the fuel and oxidant in a closed system. Additional missions for passive fuel cells include stratospheric surveillance aircraft and autonomous submersibles.

Proton Energy Systems began developing unitized regenerative fuel cells (URFC), cells that can function alternately as electrolysis cells and fuel cells, in the late 1990s. When applications for closed, dead-ended, hydrogen-oxygen primary fuel cells elevated in importance, Proton realized that its base URFC technology could easily be adapted for primary fuel cell performance. Through programs funded by OSD, MDA, and NASA, Proton completed initial demonstrations of a passive PEM fuel cell that could utilize 100 percent of the reactants. With the most recent funding from NASA, Proton is taking a two-step approach for advancing the passive PEM fuel cell. First, single-cell testing will seek to optimize the membrane-electrode-assembly for power density and dead-ended stability. Second, scale-up to relevant multi-cell configurations will demonstrate higher total stack power. The performance of the cell will be described, and the initial test data will be reported.

510. Advanced Nanocomposite Membranes for High Pressures PEM Electrolyzers

Michael Pien, Marvin Warshay, Steve Lis and Radha Jalan, ElectroChem, Inc., Woburn, MA

Advanced Regenerative Fuel Cell (RFC) energy storage systems are needed by NASA in a wide range of exploration mission applications. Primary fuel cells and water electrolyzers are the two major constituent subsystems of the RFC and have challenges for maximizing the energy storage density. Being able to operate the electrolyzer subsystem at high pressure is one of the keys to achieving the goal of maximum energy storage density. The point of operating a Polymer Electrolyte Membrane PEM electrolyzer at high pressure is that it eliminates the parasitic energy lost for external gas compression prior to high pressure reactant storage. The drawback of high-pressure operation of a PEM electrolyzer, however, is an increased diffusion of reactants across the polymer electrolyte membrane in the cell which dramatically decreases the cell efficiency.

ElectroChem has specifically developed an advanced polymer electrolyte membranes through a nanocomposite membrane technology that the membrane can perform the water electrolysis while preventing reactant gas crossover at high pressure operation up to 2,000 psig.

The developed advanced polymer electrolyte nanocomposite membranes have shown significantly reduced hydrogen crossover more than the regular Nafion polymer membranes indicating that the applying of nanocomposite structure significantly decrease hydrogen permeation. Furthermore, the conductivities of the advanced proton exchange membranes only reduced 20-25% compared to Nafion Membranes. When the nanocomposite membranes were tested as a membrane electrode assembly (MEA), the electrochemical performance of the nanocomposite membranes is not much different than that of a regular MEA made of a Nafion membrane.

511. A High-Pressure Dual-Feed Water Electrolyzer for Extraterrestrial Energy Storage

Christopher Eldridge[1], Robert J. Roy[1], John Graf[2], Mark Hoberecht[3], Sri R. Narayan[4], Andrew Kindler[4], T.I. Valdez[4] and Adam Kisor[4], (1)Energy, Space & Defense, Hamilton Sundstrand, Windsor Locks, CT, (2)NASA-JSC, Houston, TX, (3)NASA Glenn Research Center, Cleveland, OH, (4)Electrochemical Technologies, Jet Propulsion Laboratory, Pasadena, CA

High pressure oxygen and hydrogen play a critical role in the Vision for Space Exploration. Under the Exploration Systems Program, high pressure hydrogen and oxygen is needed for energy storage in regenerative fuel cells (RFC), crew life support, In-Situ Resource Utilization (ISRU) propellant production, and materials processing. Electrolysis of water based on proton exchange membrane (PEM) cell technology is the most viable for generating oxygen and hydrogen at high pressures. Development of a balanced pressure PEM cell with the capability to handle the full operating pressure as differential provides the potential for reduced system complexity and enhanced overall safety of the water electrolyzer. Furthermore, the integration of a PEM electrolyzer with a PEM fuel cell in an RFC system requires a comprehensive fluid management strategy to safely handle dissolved products in the water streams.

Hamilton Sundstrand (HS) has designed a dual-feed PEM electrolyzer capable of producing 2000 psia oxygen and hydrogen and withstanding the maximum operational pressure as differential. A two-cell stack assembled at HS with advanced membrane and electrode assemblies (MEA) fabricated at the Jet Propulsion Laboratory (JPL) will be integrated into a high pressure test stand to evaluate the assembly under various conditions of pressure and temperature from ambient to 2000 psia and 80°C, respectively. Performance parameters including the voltage and current efficiency of the prototype stack will be evaluated so NASA can generate a performance map for the design of RFC systems.

Energy Storage and Energy Conversion: Bioelectrocatalysis

Organizer: James Burgess Case Western Reserve University, Cleveland, OH

512. Citric Acid Cycle Enzymatic Cascade for Anodic Bioelectrocatalysis

Shelley Minteer and Daria Sokic-Lazic, Chemistry, Saint Louis University, St. Louis, MO

The citric acid cycle is one of the main metabolic pathways living cells utilize to completely oxidize biofuels to carbon dioxide and water. The goal of this project was to immobilize the enzymes of the citric acid cycle on a bioanode in order to oxidize ethanol to carbon dioxide for biosensor, bioreactor, biofuel cell applications. Most of the enzymes employed for the biomimic of the citric acid cycle are $NAD(P)^+$-dependent. During the oxidation of the fuel, this coenzyme is reduced to NAD(P)H. Since NAD(P)H oxidation occurs at a high overpotential at carbon electrodes an electrocatalyst, poly(methylene green), is employed to modify the electrodes to promote efficient NAD^+ regeneration. Dehydrogenase enzymes (known to be the electron producing enzymes of the Kreb's cycle) are immobilized in cascades along with non-energy producing enzymes necessary for the cycle to progress. Results obtained from the biofuel cell used in this study have shown an increase in power density with each additional dehydrogenase immobilized on an electrode surface.

513. Consolidated Bioprocessing Technologies Using Microbial Fuel Cells Powered by Microbial Consortia

Gemma Reguera, Allison Speers, Kwi Kim and Jenna Young, Microbiology and Molecular Genetics, Michigan State University, East Lansing, MI

In nature, microbial consortia carry out many energy conversion reactions using insoluble terminal electron acceptors, a process that could be harnessed to convert chemical energy into electricity in devices known as microbial fuel cells (MFCs). We have reproduced in consortia-driven MFCs energy conversion reactions from light and lignocellulose substrates that are based on interspecies H_2

transfer and organic acid transfer to the electricigen *Geobacter sulfurreducens*. In the first consortium, photosynthetic cyanobacteria produce H_2 to drive electricity production by *G. sulfurreducens*. In the second, consortia with consolidated bioprocessing organisms that degrade and ferment lignocellulose substrates results in ethanol and electricity production at high yields. Furthermore, a combination of genetic engineering and adaptive evolution approaches demonstrated that process level manipulation of the partner organisms effectively modulates the metabolic interactions within the consortia to customize and optimize the energy conversion reaction and the overall energetic yields of the process. These studies demonstrate that defined microbial consortia and genetic engineering can be used to develop efficient consolidated bioprocessing technologies in MFCs for biofuel and/or bioelectricity generation.

514. Insights From Voltammetry of Electrode-Reducing Bacteria Under Nonturnover Conditions

Daniel R. Bond, Ying Liu, Edward LaBelle, Jeffrey Gralnick and Daniel Baron, Biotechnology Institute, University of Minnesota, St. Paul, MN

Voltammetry in the presence and absence of substrates shows that bacteria such as *Geobacter sulfurreducens* and *Shewanella oneidensis* have natural mechanisms that solve many key issues common to enzymatic fuel cells. For example, by analyzing films containing only the first cells to colonize surfaces (sub-monlayers), it can be shown that *Geobacter* quickly brings redox proteins in contact with electrodes, allowing cellular oxidative machinery to operate near its maximum rate, while attached *Shewanella* cells still demonstrate a bottleneck at the cell-electrode interface, requiring mediators to facilitate rapid electron transfer. As cells stack on top of one another, akin to loading enzymes in a matrix, these organisms also demonstrate significant differences in terms of their ability to relay electrons between cells, and to the cell-electrode interface. Voltammetry in the absence of substrates has provided new insights into the nature of electron transfer as cells transition from single to multicellular thickness.

515. Electrochemical Impedance Analysis of Mediated Enzymatic Electrodes

Scott Calabrese Barton and Deboleena Chakraborty, Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI

Electrochemical impedance spectroscopy (EIS) is a powerful technique for analysis of reacting systems with combined reaction and transport phenomena on multiple time scales. EIS has been applied extensively to a wide range of electrochemical systems but has not received significant attention in systems employing mediated biocatalysts. This talk will describe the advantages and limitations of EIS as a tool for analysis and design of such electrodes, using laccase-catalyzed oxygen reduction as an example.

516. Insights From Voltammetry of Early Vs. Late Stage Biofilms of Electrode-Reducing Bacteria

Daniel R. Bond, Ying Liu, PhD, Daniel Baron, Edward LaBelle, Jeffrey Gralnick and Rhonda Franklin, Biotechnology Institute, University of Minnesota, St. Paul, MN

Voltammetry in the presence and absence of substrates shows that bacteria such as Geobacter sulfurreducens and Shewanella oneidensis appear have natural mechanisms that solve many key issues common to enzymatic fuel cells. For example, by analyzing films containing only the first cells to colonize surfaces (sub-monlayers), it appears that Geobacter quickly brings key redox proteins in contact with electrodes, allowing cellular oxidative machinery to operate near its maximum rate, while Shewanella still demonstrates a bottleneck at the cell-electrode interface, requiring mediators to facilitate rapid electron transfer. As cells stack on top of one another, akin to loading enzymes in a matrix, these species also demonstrate significant differences in terms of their ability to relay electrons between cells, and to the cell-electrode interface. Voltammetry in the absence of substrates has provided new insights into the nature of electron transfer within these films as they transition from sub-monolayer to multicellular thickness.

517. Stabilized Lithium Metal Powder (SLMP^{TM}) – Material and Application Technologies for High Energy Li Batteries

Marina Yakovleva, Brian Fitch, Yangxing Li and Yuan Gao, Lithium Division, FMC Corporation, Bessemer City, NC

It has become clear that though limited options still exist to marginally increase the energy density of the present Li-ion batteries, new approaches are needed to advance its application into the area of large format batteries, for example, HEV/PHEV/EV automotive markets. FMC's advanced material, Lectro Max Powder (SLMP) enables a new generation of Li-ion batteries by providing an independent source for lithium, which opens up choices for both anode and cathode materials. Introducing lithium in a stabilized powder form with the anode host material, such as Si and Sn-based, to form a lithium-ion system leads to a higher energy battery with more efficient utilization of lithium. Using non-lithium providing cathodes like manganese, vanadium or other metal oxides and metal fluorides that are more overcharge tolerant and potentially have lower costs, leads to safer and cheaper batteries. When used in combination, these materials can potentially double the energy density of the current lithium-ion battery.

This presentation will focus on the enabling aspect of Stabilized Lithium Metal Powder Technology (SLMP^{TM}) that provides an independent source of lithium into the Li-ion systems with emphasis on application techniques. In general, there are two common methodologies for introducing SLMP into the cell 1) surface application where an SLMP suspension is applied to the prefabricated anode sheet and 2) slurry application, where conventional electrode preparation method is employed and both binder and solvent must be compatible (non-reactive) with lithium.

Characterization of Lunar Regolith and Simulants

Sponsor: NASA Lunar Dust Mitigation Project
Organizer: James R. Gaier NASA-GRC, Cleveland, OH
Presider: James R. Gaier NASA-GRC, Cleveland, OH

Session Overview: A return to the moon within the next dozen years prompts an examination of potential opportunities and hazards. Lunar regolith (or "soil") is both an important source of resources and a material that can degrade our capabilities to explore. This session seeks papers describing the chemical properties of both the lunar regolith and of lunar regolith simulants, with an emphasis on how those properties could affect the success of lunar missions.

518. The Lunar Regolith and the LHT Series of Regolith Simulants

Douglas B. Stoeser and Stephen A. Wilson, U.S. Geological Survey, Denver, CO

NASA has made the decision to put a base at one of the lunar poles by 2024AD. The regolith of the North Pole is comprised dominantly of highlands material with a minor amount of KREEP and mare whereas the South Pole, located on the southern rim of the SPA basin, consists of upper crustal highlands material with minor amounts of lower crustal (SPA) material. The polar base decision, along with some of the precursor missions, places emphasis on developing highlands type regolith simulants. In response, NASA in partnership with the U.S. Geological Survey is developing the NU-LHT (NASA/USGS-Lunar Highland Type) simulant series. Because Apollo 16 is the only highlands site for which we have good sample representation the LHT series is compositionally matched to average Apollo 16 regolith. Four prototype simulants have been prepared to date, LHT-1M, 1D, 2M, and 2C (C-coarse <10 cm, M-medium <1mm, and D-dust <50µm). LHT-2M represents a significant advance over previous simulants in that it utilizes ten components including norite and anorthosite feedstocks from the Stillwater Complex, MT, synthetic agglutinate, other glass, olivine, and minor minerals (ilmenite, synthetic whitlockite, fluorapatite, pyrite, chromite). LHT-2C consists of 2M simulant mixed with synthetic impact melt breccia clasts for the coarse (>1mm) fragments. New directions for the project include development of LHT-3M, natural and synthetic mineral feedstocks (plagioclase, pyroxene, and olivine), and a synthetic materials based regolith simulant.

519. Industrial Scale Manufacturing of Lunar Simulant Components From Oxides with Remotely-Coupled Transferred Arc Plasma

Michael Weinstein, Zybek Advanced Products, Inc., Boulder, CO

Lunar simulants are a core requirement with applications across many NASA and commercial space exploration programs. Most lunar simulants available for research are made from mined materials. These materials are then sized and blended to match the desired properties. The starting chemistries are essentially the same for the finished product. Contaminates, such as Chlorine and excess Sodium, can cause experimental challenges and differences in final material performance.

Zybek has a developed a process for creating 'synthetic' minerals from low-cost, commercially available oxides. For example, ZAP is manufacturing AN100 Anorthite ($CaAl_2Si_2O_8$) from commercially-available batch ingredients (i.e., CaO, Al_2O_3, SiO_2). The batch ingredients are mixed in proper ratios and brought to molten temperatures by a transferred arc plasma. The molten material is then cooled with a means that promotes crystal growth. The crystals are then milled with a Pulse mill that breaks material along grain. The resulting material size is 1 to 500 micron. If a glass is required, the molten material is quenched rapidly.

The process has also been demonstrated for other materials, including: Albite / Anorthite blends, Augite, Pigeonite, Fayalite, and synthetic Ruby.

The plasma-based process and pulse mill used to manufacture lunar simulants and dust materials will be discussed in the presentation. Data on the final chemistries of these synthetic minerals will be presented along with photos of the grain structure.

520. Synthesis and Stability of Iron Nanoparticles for Lunar Environment Studies

Ching-cheh Hung and Jeremiah McNatt, NASA Glenn Research Center, Cleveland, OH

Simulant of lunar dust is needed when doing research of the lunar environment. However, unlike the true lunar dust, today's simulants do not contain nanophase iron. Two different processes were developed to fabricate nanophase iron to be used as part of the lunar dust simulant. The two processes are: (1) Sequentially treating a mixture of ferric chloride, fluorinated carbon, and soda lime glass beads at about 300°C in nitrogen, at room temperature in air, and at 1050°C in nitrogen. The product includes glass beads that are grey in color, can be attracted by a magnet, and contain ɑ iron nanoparticles (which seem to slowly lose their lattice structure in ambient air during a period of 12 months). This product may have some similarity to the lunar glassy regolith that contains Fe^0. The other process is: (2) Heating a mixture of carbon black and a lunar simulant (a mixed metal oxide that includes iron oxide) at 1050°C in introgen. This process simulates lunar dust reaction to the carbon in a micrometeorite at the time of impact. The product contains a chemically modified simulant that can be attracted by a magnet and has a surface layer whose iron concentration increased during the reaction. The iron was found to be ɑ iron and Fe_3O_4 nanoparticles, which appears to grow after the fabrication process, but stabilizes after 6 months of ambient air storage.

521. Suitability of Lunar Regolith Simulants for Development of Lunar Processing Equipment

Kenneth W. Street, Tribology and Mechanical Components Branch, The NASA-Glenn Research Center, Cleveland, OH, Chandra S. Ray, Materials Research Center, Missouri University of Science and Technology, Rolla, MO and Douglas L. Rickman, Global Hydrology and Climate Center NSSTC, NASA-Marshall Space Flight Center, Huntsville, AL

The return to the moon is providing a number of challenges for development of lunar regolith processing equipment. There are no metal ore deposits as on Earth, no oxygen atmosphere and no readily available water sources on the moon. During the Apollo missions, lunar explorers stayed only a few days on the surface. All materials for environment and sustenance were brought with the explorers during each mission. The proposed return is based around longer missions leading to a continuously manned lunar outpost. Various chemical processes have been developed to extract oxygen and metals from lunar regolith, many of which are based around high temperature reactions involving molten regolith. These processes have been developed and tested using terrestrial analogues of the regolith minerals which have been hydrothermally altered when formed on earth. As a result, the melting points and water content of terrestrial analogues do not match those of lunar feedstock. Melting temperature is of concern in choosing construction materials and in determining energy budget for these processes. Water content is important for processes that produce water – the lunar analogues used to produce water will have very different yields than terrestrial pilot materials that may contain significant water already. To this end we have undertaken various studies of lunar regolith simulants to determine if the simulants are suitable substitutes for production of various key components for human survivability during sustained presence on the moon.

522. Surface Energy of Lunar Soil Simulants

R. Allen Wilkinson, Fluid Physics and Transport Branch, NASA-Glenn Research Center, Cleveland, OH and Kenneth W. Street, Tribology and Mechanical Components Branch, The NASA-Glenn Research Center, Cleveland, OH

Regolith on the lunar surface has a notable cohesion as described by Apollo astronauts. Particle cohesion and adhesion are crucial to dust mitigation, tool-soil interaction and bulk soil strength affecting excavation or material handling with chutes and hoppers. Since there are other attachment forces like coulombic and image charge attractions that can play a roll it is important to account for all the relevant physical causes when modeling or attempting to remove or repel particles from a surface. No direct measurements of cohesion or adhesion in lunar regolith have ever been made, although the adhesion energy of regolith stuck on the surface of the returned Lunar Surveyor 3 excavator bucket provided an estimate. Work presented here uses inverse gas chromatography (IGC) to measure the dispersive and polar components of surface energy associated with the Hammaker constant of van der Waals forces of fine-grained particulates. In preparation for such measurements on pristine lunar regolith in NASA storage the authors measured the surface energy of three lunar regolith simulants: JSC-1a, a maré basaltic simulant, NU-LHT-2M and OB-1, both anorthsitic lunar highlands simulants. The measurements were made at 30 degrees Centigrade under He background gas with and without pre-conditioning at 105 degrees Centigrade. The resulting surface energies will be presented along with a measure of the repeatability.

523. Thermal, Chemical and Plasma Activation of JSC1a-Fines

Randy L. Vander Wal, Ph.D.[1], Michael J. Kulis, Ph.D.[2], Gordon M. Berger[2] and Kenneth W. Street[3], (1)Energy and Mineral Engineering, Penn State University, University Park, PA, (2)NASA-Glenn, The NCSER, Cleveland, PA, (3)Tribology and Mechanical Components, The NASA-Glenn Research Center, Cleveland, OH

Realistic lunar simulant is needed to pre-test surface systems, for in situ processing, to design wear-resistant materials and to develop mitigation strategies. A critical feature of such simulants is "activity" – broadly defined as reactivity by virtue of lattice vacancies and surface radicals and free charge carriers. Here, thermal, chemical and plasma activation are explored with the resulting

activation measured by simulant conductivity for JSC-1a fines.
For thermal and chemical activation, results are compared both isothermally and across a broad range of temperatures. Time constants and activation energies are established for each process. Significantly, activation/deactivation is found to be reversible highlighting preservation of the simulant's physical characteristics.
A plasma activates JSC-1a fines in the form of a point-to-plane corona discharge. Comparison of the deactivation data to Langmuir adsorption yields a passivation rate (by oxygen) that is much slower than the gas-kinetic surface collision rate. Significantly, passivation may be interrupted to maintain the simulant in an intermediate degree of activation.
Occurring at the sample surface, terminating groups and lattice oxygen atoms are removed. These processes increase the charge carrier concentrations by liberating bonding electrons and creating radical sites. Additionally, potential barriers between particles and grains decrease. Accordingly, changes in the sample conductivity provide a measure of the degree of activation. Deactivation through chemisorption fills vacancies, terminates radical sites and depletes free charge thereby leading to reduced conductivity.

524. Particle-Size Dependent Bipolar Charging of Regolith Simulant

Keith M. Forward, Daniel J. Lacks and R. Mohan Sankaran, Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH

The intense dust devils and dust storms on Mars are believed to generate extensive electrostatic effects. To understand these phenomena, we carry out experiments on the triboelectric charging of Martian regolith simulant (JSC-1 Mars). In our experiment set-up, a fluid flow apparatus is used such that only particle-particle interactions occur, as is the case in Martian dust events. Our experiments directly show the charge behavior to be characterized by smaller particles charging negatively and larger particles charging positively. This particle-size dependence of charge polarity underlies the charge separation that generates electric fields in Martian dust events.

Chemical Biology & Medicinal Chemistry (2)

Organizer: Gregory Tochtrop Case Western Reserve University, Cleveland, OH
Presider: Gregory Tochtrop Case Western Reserve University, Cleveland, OH

Session Overview: This session will span the chemistry biology spectrum, and focus on the design, synthesis, and evaluation of small molecules against biological systems.

525. Small Molecule Transcriptional Switches

Anna K. Mapp, Department of Chemistry University of Michigan, University of Michigan, Ann Arbor, MI

Altered transcriptional patterns are associated with all human diseases, either as the cause of the disease or as an effect. For this reason, molecules that interfere with or promote protein-protein interactions within the transcriptional regulatory network are exciting targets for therapeutic development and as mechanistic probes. A primary challenge in this effort is that there is little molecular-level detail regarding these protein-protein interactions. We have found that small, amphipathic heterocycles are excellent mimics of one class of natural transcription factors and can be used as transcriptional switches. When the molecules are targeted to a specific gene, they function as activators, up-regulating transcription. Small changes to the structures convert them into inhibitors of transcription, an 'off switch'. In once instance, we use these molecules to turn off expression of a cell surface growth receptor that is up-regulated in many breast cancers.

526. Zwitterionic Polysaccharides for a Complete Carbohydrate-Based Vaccine

Peter Andreana, Assistant Prof. Chemistry, Chemistry, Wayne State University, Detroit, MI

Vaccines are powerful tools for disease prevention and various cell surface carbohydrates are important templates for their development. However, as isolated single entities carbohydrates have only been known to invoke T-cell-independent immune responses. To elicit a strong and long-term immunity, a vaccine must target the class II major histocompatibility complex (MHCII) and CD4+ T-cells in a T-cell-dependent cascade. Most recently zwitterionic polysaccharides were isolated from anaerobic bacteria and shown to modulate the cellular immune system by activating CD4+ T-cells via MHCII. Based on this discovery and as an alternative approach for vaccine development, we hypothesize that chemically conjugating tumor associating carbohydrate antigens/haptens (TACAs) to zwitterionic polysaccharides (ZPS) will lead to T-cell-dependent vaccines.

This talk will focus on the isolation, purification, chemical modification of PS A1 (a naturally occurring capsular polysaccharide) and subsequent in vivo mouse studies with a carbohydrate cancer antigen (Tn) conjugated to PS A1. The results will demonstrate that an IgG immune response is specific for Tn antigen highlighting an MHCII mediated immune response.

527. Breaking Down Barriers: Disrupting the Integrity of the Mycobacterial Cell Envelop.

Donald R. Ronning, Ph.D., Chemistry, The University of Toledo, Toledo, OH

The emergence of multi-drug resistant strains of the mycobacterium responsible for Tuberculosis infection emphasizes the need for new treatment. Among the validated drug targets of /Mycobacterium tuberculosis/, enzymes involved in the maintenance of the cell wall are a main focus in tuberculosis drug development. Indeed, it is expected that the disruption of the primary physical barrier protecting mycobacteria would be bactericidal. The antigen 85 family of enzymes are central in maintaining cell wall integrity through their mycolyltransferase activity, and therefore represent an attractive antimycobacterial drug target. The reasons behind the existence of three enzymes with identical structures remain unclear. A better understanding of the substrate specificity as well as the mechanism of the mycolyltransfer is necessary to the development of possible drugs inhibiting the enzymes. Recent progress in the structural and enzymatic characterization of this family of enzymes will be presented.

528. Synthesis of Biologically Active Heterocycles

Jetze J. Tepe, Chemistry, Michigan State University, East Lansing, MI

Our program is focused on the development of new and diverse classes of small natural product-like scaffolds capable of modulating a variety of signaling pathways prevalent to the treatment of cancer and inflammatory diseases. To achieve this goal we have developed several new heterocyclic methodologies using a general oxazolone template to access highly substituted scaffolds. Our main synthetic criteria include the control of stereochemistry, product diversity and applicability to the total synthesis of biologically active natural products and derivatives thereof. This seminar will be focused on the synthetic methods and the biological applications of some of these scaffolds.

529. N(epsilon)-Thioacetyllysine as a Multifaceted Chemical Probe for Protein Deacetylase-Catalyzed Reactions

Weiping Zheng, Department of Chemistry, University of Akron, Akron, OH

The family of protein deacetylase enzymes can catalyze the specific lysine N(epsilon)-deacetylation on proteins such as the core histone proteins, various transcription factors, alpha-tubulin, and acetyl-coenzyme A synthetases that are respectively involved in gene transcriptional, cytoskeletal, and metabolic control. This deacetylation reaction represents an integral component for an emerging intracellular signaling mechanism defined by the protein posttranslational reversible lysine N(epsilon)-acetylation and deacetylation, and has been targeted for developing novel therapies for metabolic and age-related diseases and cancer. This presentation will be focused on our studies employing N(epsilon)-thioacetyllysine as a multifaceted chemical probe for this enzymatic protein lysine N(epsilon)-deacetylation reaction. In specific, the judicious use of N(epsilon)-thioacetyllysine has resulted in (i) the development of the first spectrophotometric assay selective for the class I

Zn^{2+}-dependant protein deacetylase enzyme HDAC8 that holds potentials for not only inhibitor screening but also selective activity reporting for HDAC8 activity; (ii) the establishment of replacing N(epsilon)-thioacetyllysine for N(epsilon)-acetyllysine as a simple yet general and very efficient inhibitory strategy against the class III NAD^+-dependant protein deacetylase enzymes (or sirtuins); and (iii) the structural elucidation of the first catalytic intermediate step for the sirtuin-catalyzed deacetylation reaction. While these results have demonstrated the unique utility of N(epsilon)-thioacetyllysine as a chemical probe for protein deacetylase-catalyzed lysine N(epsilon)-deacetylation reaction, it is hoped that its use will further promote our fundamental understanding and pharmacological exploitation of protein deacetylase-catalyzed reactions including the deacetylation reaction and the ADP-ribosylation reaction that many sirtuins are also able to catalyze.

530. Oxidative Stability and Characterization of Physiologically Relevant Fatty Acids by Calorimetric and Dielectric Analysis

Hoi Ling Cheung, BS, Yazid Hussein, Ibrahim Abdelfattah, Dr. Kenneth S. Alexander and Dr. Alan Riga Riga, Department of Chemistry, Cleveland State University, Cleveland, OH

Fatty acids are relevant to human life. The majority of biomaterials are comprised of polyunsaturated fatty acids (PUFA); the PUFA are concentrated in the cell membrane and nervous tissue. Free fatty acids (FFAs) are active metabolically and are precursors for prostaglandins. Fatty acid chemistry may be involved in inflammatory, neurological, metabolic, neoplastic, immunological and cardiovascular diseases. The high distribution of fatty acids and associated pathologies warrant investigation of the oxidative and physical properties of these critical acids. We focused on the following physiologically relevant FFAs: oleic, linoleic, and linolenic.

Differential Scanning Calorimetry (DSC) of FFAs was used to determine the Oxidation Onset Temperature, relative oxidative stability, ASTM E2009, as well as, the transition temperatures and heats of fusion and crystallization. The Oxidation Onset Temperature decreased with increasing double bond content with a R^2 of 0.98. Beta oxidation is the mechanism for the oxidative process. It appears that the observed melt temperature of the unsaturated acids decreases with increasing double bond content, from one to three sites of unsaturation. Another focus of this study is to evaluate the FFAs by Dielectric Thermal Analysis (DEA) as a function of temperature and frequency. The DEA properties of the air aged liquid FFAs indicate that the electrical conductivity and complex permittivity can be correlated with the degree of unsaturation or double bond content. The probable conduction mechanism of the dipolar and oxidized “particles” follows the “Polaron Theory” or “Hopping Conduction Model” with the electron dense areas surrounding the double bonds as conduction pathways.

Chemical Education: K-12 Level

Sponsor: ACS Division of Chemical Education (DivCHED)
Organizer: LaRuth McAfee Case Western Reserve University, Cleveland, OH
Presider: LaRuth C. McAfee, PhD Case Western Reserve University, Cleveland, OH

Session Overview: The first half of the session will feature presentations on current topics in K-12 chemical education. These will include updates on electronic resources to aid in teaching chemistry, and outreach programs that have been developed to promote and strengthen pre-college chemistry education. The second half of this session will feature a panel discussion and activities led by administrators, teachers, and students who work at or attend STEM high schools in Ohio. They will share how large-scale (school/district-wide) changes in STEM education have promoted academic innovation and success in chemistry, as well as in other STEM fields.

531. ACS National Historic Chemical Landmarks Website

Janan M. Hayes, Merced College - retired, Sacramento, CA

One of the American Chemical Society's best kept secret teacher supplemental aids is the National Historic Chemical Landmarks (NHCL) program. But now with the introduction of a new interactive website, www.acs.org/landmarks, teachers, students and all inquiring minds have an opportunity to learn more of the chemically related achievements to the advancement of society. Learn more about Scotch Tape, Jamestown Colony, Tide detergent, and many other NHCL sites. Plus, now there are maps, a timeline, puzzles and games in addition to extensive write up about the landmarks. Come, see, and go home with a new informational resource from ACS.

532. ChemSource: A Groundbreaking Concept Charting a New Course

Mary Virginia Orna, Department of Chemistry, College of New Rochelle, New Rochelle, NY

ChemSource was a late 20th-century ground-breaking concept that brought together teams of experienced teachers at all levels to produce a comprehensive resource for pre-service and in-service chemistry teachers that continues to have an important impact in chemistry education 15 years out! There have been many changes in education in the intervening years. Among them are widespread adoption of national and state standards, emphasis on inquiry, especially in the laboratory, and greater attention to both formative and summative assessment. This paper will illustrate how ChemSource is presently being adapted to meet the needs of today's teachers and students.

533. Project REEL In Advanced Placement Chemistry

Ted M. Clark, Department of Chemistry, the Ohio State University, Columbus, OH and **Brian M. Urig**, Science, Oxford High School, Oxford, PA, Oxford, PA

Although the content and laboratory program in Advanced Placement (AP) Chemistry exceeds that of traditional high school courses, AP students lack exposure to authentic research experiences. The AP Chemistry curriculum at Oxford Area High School is one site where an AP Chemistry course is being modified to include aspects of modern scientific research that was developed as part of Project REEL (Research Experiences to Enhance Learning). Preliminary results from this collaboration have been positive. In addition to strengthening the content and laboratory experiences within the AP Chemistry curriculum, 40% of the students who have completed the program plan to pursue chemistry or closely related fields in college. Incorporating REEL also serves as a "recruiting" tool to entice and retain talented science students. Within this presentation we will discuss this novel High School-University collaboration.

534. Chemistry and Hip Hop: Outreach Efforts to Attract Minority Students to the Chemical Sciences

Sibrina Collins, Department of Chemistry, College of Wooster, Wooster, OH and Juan E. Gilbert, Department of Computer Science and Software Engineering, Auburn University, Auburn, AL

Our efforts focus on providing "targeted presentations" drawing parallels between the chemical sciences and the Hip Hop industry. We believe this approach can be very effective, specifically using Hip Hop as a "hook" to attract underrepresented minority high school students to the chemical sciences. Moreover, using this approach to chemical education, we are raising a public awareness and appreciation for the chemical sciences. Recent outreach efforts will be discussed.

535. Project-Based Learning Techniques in STEM High Schools

Jeffrey D. McClellan, MC2STEM High School, Cleveland Metropolitan School District, Cleveland, OH and Marcy Raymond, Metro Early College High School, Columbus, OH

This discussion will be led by students, teachers, and administrators from two STEM high schools in Ohio: the MC2STEM High School in Cleveland and the Metro Early College High School in Columbus. Presenters will open with an overview of how the schools approach science education in ways that are different from a traditional high school pedagogical method, with a special emphasis on chemistry. This will be followed by an interactive activity to allow the audience to experience the types of projects students are assigned at these schools. Finally, the session will conclude with a panel discussion that will allow the STEM high school representatives to answer any questions from the audience.

Organic Chemistry: Cope Scholar Symposium

Sponsor: ACS Division of Organic Chemistry, Quanta BioDesign, Ltd., Toledo Section of the ACS
Organizer: Kana Yamamoto University of Toledo, Toledo, OH
Organizer: Steven J. Sucheck University of Toledo, Toledo, OH
Presider: Kana Yamamoto University of Toledo

Session Overview: This symposium will be in honor of Professor Melanie Sanford from the University of Michigan, recipient of a 2008 Cope Scholar Award. Professor Sanford has established herself as a leader in the field of organometallic chemistry, in particular C-H bond activation. C-H Bond activation has numerous applications in green chemistry, and the transformations have been applied to preparation of many types of functional molecules. One noticeable achievement of her research is on the recognition of new type of palladium catalytic cycle, which shuttles between previously unrecognized oxidation states. Although palladium chemistry is considered a matured field, her discovery has opened a new mode of reactivity that could lead to application into non-traditional transformations. The subject of Professor Sanford's talk will be an overview of the current status of her findings. In addition the symposium will feature a number of invited talks from emerging young investigators throughout the Midwest region.

536. Controlled Syntheses of π-Conjugated Polymers: Mechanism and New Microstructures

Anne J. McNeil, Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, Ann Arbor, MI

π-Conjugated polymers are the principal components in emerging technologies due to their beneficial properties, including the ability to synthetically tune the optical and electronic character, their low materials cost, and their facile deposition using solution processing. Recent studies have shown that the nanoscale organization in polymer films may be as important as the π-conjugation in terms of device performance. Surprisingly, there have been few studies aimed at controlling these phase separation processes, in part due to the limited number of polymer architectures available. Recent reports of controlled chain-growth synthesis of π-conjugated polymers using nickel and palladium catalysts have revitalized the search for new materials with specific thermodynamic and optoelectronic properties. This talk will highlight our efforts towards a mechanistic understanding of these chain-growth polymerizations, their utilization in the syntheses of new π-conjugated copolymers with unique microstructures, and the implications for their use in emerging technologies.

537. Selective Aqueous-Phase Adhesion by Molecularly Engineered Materials

Dennis Bong, Department of Chemistry, The Ohio State University, Columbus, OH

Multivalency and pre-organization are fundamental aspects of molecular recognition at the lipid membrane-water interface and can render weak monomeric binding interactions selective and robust; this concept is important throughout biology, biotechnology and materials science. We have discovered that the non-native small molecules cyanuric acid and melamine can effectively modulate lipid
interactions by hydrogen-bonding in aqueous milieu. The aqueous phase recognition of cyanuric acid (CA) and melamine (M) lipid derivatives remains robust and selective; this motif appears under-utilized in materials design. This work is notable and of general interest given the few detailed studies of aqueous phase hydrogen-bonding systems. This system has been characterized

structurally by cryo-EM and functionally by fluorescence methods and titration calorimetry. Furthermore, we have found that the designed lipid-lipid headgroup interactions result in dramatic alteration of the lipid phase morphology, providing insight into the coupling of molecular interactions with assembly state. As such, this work contributes to our understanding of fundamental phenomena such as molecular recognition at the lipid-water interface, membrane chemistry and has possible biomedical and materials applications with regard to selective surface adhesion.

538. Shake It up! Chemistry through High Speed Ball Milling”

William C. Shearouse, Daniel C. Waddell, **James Mack**, Dennis A. Fulmer and Indre Thiel, Department of Chemistry, University of Cincinnati, Cincinnati, OH

Solvent has been considered a necessity in chemical reactions since the days of Aristotle. Even today it is believed that reactions conducted in solution are faster, more efficient and show greater reproducibility than those in the solid state. Because of this, chemists have been trained to use solution phase chemistry in organic synthesis to such an extent that solid state chemistry is not considered. However, due to increasing interest in environmental protection and waste minimization, solvent-free chemistry has recently gained momentum. High speed ball milling (HSBM) has been developed as a solvent-free technique which may potentially rival solution phase chemistry. HSBM has been demonstrated to be equally fast, efficient and as reproducible as solution phase chemistry. HSBM can be conducted under a variety of conditions, mimicking solution phase chemistry for a variety of chemical reactions and procedures. Although methods have been developed to trap and dispose of solvent waste more efficiently, the ideal situation is to avoid generating the waste completely. In our research laboratory, we have developed safer, more environmentally benign method for reductions and oxidations using HSBM. We have studied multi-component reactions and enolate chemistry via this novel methodology.

539. Zinc-Mediated Palladium-Catalyzed Formation of Carbon-Sulfur Bonds

James P. Stambuli and Chad C. Eichman, Department of Chemistry, The Ohio State University, Columbus, OH

The presence of a catalytic amount of zinc chloride in combination with a palladium catalyst ligated by a monodentate phosphine allows the coupling of aryl and alkyl thiols with aryl bromides in high yields. In the absence of the zinc salt, the same catalyst fails to produce the desired sulfide product. These results describe the first high-yielding and general monodentate phosphine-ligated palladium catalyst for the formation of biaryl and alkyl aryl sulfides. Importantly, the addition of a catalytic amount of zinc chloride to a palladium catalyst system that reportedly failed to promote the formation of sulfide product, allows this once ineffective catalyst system to provide the sulfide product in good yield. Thus, this novel strategy to add a zinc co-catalyst to attenuate the reactivity of strong thiolate nucleophiles in the presence of palladium, appears to be general. The scope of this process will be presented, along with the suggested reaction mechanism.

540. Oxidation of Amino Acids, Peptides and Proteins by Iron Complexes

Jeremy J. Kodanko, Ph.D., Department of Chemistry, Wayne State University, Detroit, MI

Oxidation of Amino Acids, Peptides and Protein by Iron Complexes

Jeremy J. Kodanko

Wayne State University

Most enzyme inhibitors carry out their function by binding reversibly to a target protein. This approach is severely limited by the fact that one molecule of inhibitor can inactivate only one molecule of enzyme at a time. In other words, this inhibition is stoichiometric. A potentially more

effective approach is to develop catalytic enzyme inhibitors, molecules that are capable of inactivating multiple copies of a target protein. Considering that the oxidation of amino acid side chains and/or the backbone can result in protein inactivation, we present the oxidative modification of amino acids, peptides and proteins by synthetic iron complexes, studies directed towards the goal of developing catalytic enzyme inhibitors. High valent iron(IV)-oxo species of the general formula $[Fe^{IV}(O)(L)]^{2+}$, where L is a pentadentate ligand, oxidize the side chains and backbone of protected amino acid derivatives. Mechanistic studies, including observations of kinetic isotope effects, will be presented that elucidate reaction mechanisms with reactive substrates. A divergent synthetic method for conjugating iron(IV)-oxo complexes to peptides will be discussed, which allows multiple peptide-ligand conjugates to be prepared from a single precursor. Iron(IV)-oxo species prepared from these conjugates are stable up to several hours at room temperature, and can be quenched by an intramolecular pathway. Oxidation of peptides and proteins by synthetic iron complexes will also be presented.

541. Palladium(II/IV) Catalyzed Reactions In Organic Synthesis

Melanie S. Sanford, Department of Chemistry, University of Michigan, Ann Arbor, MI

The development of regio- and chemoselective methods for the functionalization of carbon–hydrogen bonds remains a tremendous challenge in synthetic organic chemistry, and this presentation will describe my group’s recent advances in the area. Our mechanistic approach towards the development of transition metal-catalyzed reactions has allowed the discovery and optimization of catalytic methods for the selective transformation of C–H bonds into C–O, C–Cl, C–Br, C–I, C–F, and C–C bonds under mild conditions. The scope, selectivity, and functional group tolerance of these new reactions in the context of the synthesis of biologically active molecules will be discussed.
The mechanism of these reactions is proposed to involve a Pd(II/IV) catalytic cycle. Mechanistic evidence supporting this proposal will be discussed in detail. This type of mechanistic manifold offers a number of advantages that make it highly complementary to related Pd(II/0)-catalyzed methods in organic synthesis. These include the ability access sp3 C–N, C–O, and C–X halogen bonds, the ability to generate Ar–F bonds, and the ability to circumvent competing β-hydride elimination pathways. These unique characteristics of the Pd(II/IV) catalytic cycle have led us to pursue novel Pd(II/IV)-catalyzed methods for organic synthesis. Some of these new methods, including the arylhalogenation and aminooxygenation of alkenes, the oxidative cyclization of enynes, and the fluorination of aryl metal reagents, will be discussed in detail.

Chemical Education: High School Teacher Award Symposium

Sponsor: Penn Ohio Border Section
Organizer: Doris Zimmerman Penn Ohio Border Section, Warren, OH
Organizer: Leslie McSparrin Sharpsville Area High School, Sharon, PA
Presider: Doris Zimmerman Penn Ohio Border Section, Warren, OH

Session Overview: This symposium is being given by past Central Regional Awardees in High School Chemistry Teaching - basically a "How I Do It" or "What I Do" Symposium.

542. Facts, Fallacies, Flim-Flams and the Mole-Action Pac

William E. Snyder, 2009 CRM High School Teacher Award, Penn Ohio Border Section, Poland Seminary High School, Poland, OH

Two student-centered activities, “Facts, Fallacies, Flim-Flams” and “The Mole-Action Pac” will be presented and discussed in the context of student inquiry and discovery. “Facts,Fallacies,Flim-Flams” focuses on basic atomic structure, history, and related lab experiences. Student misconceptions on this topic provide the springboard for the development of an alternative assessment called The Atomic File. “The Mole-Action Pac” introduces the concept and application of the mole through discovery-type activity stations whereby student groups gather and interpret data. The results are presented and discussed among their classroom peers. These activities are designed for introductory high school chemistry students. State and National standards are noted.

543. Ideas for Teaching Stoichiometry

Kathy Kitzmann, 1997 CRM High School Teacher Award, Detroit Section, Mercy High School, Farmington Hills, MI

Stoichiometry ~ students hate it, teachers love it! Limiting reactants ~ students understand the food analogies easily but fall apart when they see chemical formulas. The presenter will share several teaching ideas, a guided inquiry, a lab, and a classroom demonstration all related to stoichiometry and limiting reactants.

544. The Ethanol Project: A Mock Senate Hearing

Julia Winter, 2003 CRM High School Teacher Award, Detroit Section, Detroit Country Day School, Beverly Hills, MI

The different sides of the debate of whether ethanol should be developed as an alternative for fossil fuels were addressed in this unique project that incorporated role-playing, public speaking, and analytical writing. Students were each assigned various titles of people that would have an opinion on the development of ethanol and thus could be called before a United States senate sub-committee hearing. The students created a character and biography for their role and developed a position on ethanol consistent with their character. The students' work was presented both as a written paper and during a mock senate hearing in class. The final piece of the project was an in-class essay in which the students used the facts from the senate hearing to write their own personal position on ethanol. Using this multi-faceted approach, different aspects of a problem beyond the chemistry classroom were addressed. This type of project could be adapted to other science-related problems.

545. Maintaining Student Interest in Chemistry

Jesse D. Bernstein, 2004 CRM High School Teacher Award, Cleveland Section, Science Department, Miami Country Day School, Miami Shores, FL

How to better gain and maintain student interest in Chemistry? That was the question I posed to myself well over ten years ago. Since that time I have incorporated lab experiments, both Inquiry and Forensic types, along with activities that I use before vacations that have spurred or maintained student enthusiasm for chemistry. I will share some of these activities during this symposium.

546. Does Teaching Chemistry by Guided Inquiry Correct Student Misconceptions?

Leslie McSparrin, 2005 CRM High School Teacher Award, Penn Ohio Border Section, Sharpsville Area High School, Sharon, PA

ABSTRACT

The research in this study was designed to answer the research question: `Does teaching chemistry by the method of guided inquiry correct student misconceptions?` Two chemistry concepts were the focus of the study. One concept studied was the production of light by atomic emissions (including characteristic properties of both waves and light). The other concept studied was acid/base theory. A two-tiered multiple-choice pretest was administered to participants before the start of each unit. Following each unit, the same two-tiered multiple-choice test was administered as a posttest. Sixty-four students from a semi-rural high school in Northwestern Pennsylvania participated in the study across three levels of chemistry: Advanced Placement Chemistry, Chemistry I, and Conceptual Chemistry. The mean score increased in the positive direction for participants in all three levels of chemistry by the time of the posttests. In addition, many students provided answers with written responses that indicated that certain previously documented misconceptions had been corrected. Also, most of the participants were able to successfully apply the scientific method to complete culminating authentic assessments during the study. These conclusions were substantiated by both quantitative statistical data and qualitative written response and interview data. Students in Chemistry I experienced the most substantial gains among the participants. The students in this study reported that they had gained more understanding from guided inquiry activities and preferred this form of science instruction in chemistry.

547. The Chemistry of Hydroponics

Jeffrey Bracken, 2008 CRM High School Teacher Award, Columbus Section, Westerville North High School, Westerville, OH

Our science department started a hydroponics program in the fall of 2007 when our local police department donated four 1000-Watt grow lights that had been confiscated in a recent criminal investigation. What’s followed has been an exciting journey into the chemistry of plant growth. I’ll share some of our initial results and anticipated future endeavors.