
The Eleventh Annual

# Undergraduate Research Symposium

Sponsored by the Western New York Section

of the American Chemical Society

*Saturday April 28, 2018*

*University at Buffalo, SUNY*

## *Welcome Message from the Organizing Committee*

Welcome to the 11th annual Undergraduate Research Symposium hosted by the Western New York section of the American Chemical Society! The talks and posters presented today will highlight the undergraduate research taking place at institutions throughout the region, extending beyond NY into PA and southern Ontario.

Undergraduate research is often the foundation for a long-term career in the sciences and we are excited to host an event where participants can share their work in a supportive and active setting. There are a number of research topics being presented spanning all sub-disciplines of chemistry. You are encouraged to take the opportunity to network with your peers and faculty mentors in a relaxed scientific atmosphere. Whether you are presenting your work for the first time or are showcasing the latest results of an ongoing project, we hope that you find the event rewarding and informative.

This event would not be possible without all the efforts of our student researchers and we thank all of you for participating today. We are also grateful to our keynote speaker, Prof. Ellen M. Matson, from the University of Rochester for joining us in the celebration of undergraduate research. Finally, we would like to thank all of the faculty and staff that have helped organize and run the symposium and the generous support of our sponsors for providing the resources to make the event possible.

Welcome,

Timothy R. Cook and Ekin Atilla-Gokcumen

Co-chairs, 2018 Symposium Committee

## *2018 Symposium Organizing Committee*

Dr. Timothy R. Cook
Dr. Ekin Atilla Gokcumen
2018 Symposium Committee Co-chairs
Department of Chemistry, University at Buffalo, SUNY

Dr. Robyn Goacher
Department of Biochemistry, Chemistry and Physics, Niagara University

Dr. Timothy M. Gregg
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Dr. Dominic L. Ventura
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Dr. Valerie A. Frerichs
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**Keynote Speaker**

**Ellen M. Matson**

Ellen Matson received her PhD in Chemistry from Purdue University in 2013, under the guidance of Suzanne Bart. During her graduate studies, Ellen's research focused on the synthesis and reactivity of low-valent, uranium alkyl complexes. Her work culminated in two national awards; Ellen was named the 2013 recipient of the Iota Sigma Pi Anna Louise Hoffman Award for Excellence in Graduate Research, and an 2014 American Chemical Society Division of Inorganic Chemistry Young Investigator. Following graduation, Ellen performed her postdoctoral research at the University of Illinois at Urbana-Champaign, in the research group of Alison Fout. In 2015, Ellen started her independent career at the University of Rochester, where she has built a research program focused on the synthesis, reactivity and electrochemical applications of heterometallic polyoxovanadate-alkoxide clusters.

The worldwide push to generate electricity from renewable sources has created a critical need to develop improved energy storage and fuel-production strategies. Although recent advances in the conversion of solar and wind energy into electrical energy have been increasingly economical, without effective methods for storage, it is impossible to integrate these intermittent resources into the commercial sector. Research in the Matson Group focuses on using synthetic inorganic chemistry to address issues related to Energy Storage and Production. Toward accomplishing these goals, we are investigating the synthesis, characterization and reactivity of heterometallic polyoxovanadate-alkoxide clusters. These unique, multimetallic assemblies are generated in high yields via solvothermal reactions from simple molecular precursors. Notably, the polyoxovanadate subunit possesses a high degree of redox flexibility, rendering it ideal for supporting multielectron transformations of inert, gaseous substrates. Herein, we present our results related to the activation of small molecules across heterometal-functionalized polyoxovanadate-alkoxide clusters.

# Schedule of Events

April 28, 2018

*Natural Sciences Complex*
*University at Buffalo, North Campus*

| | | |
|---|---|---|
| 9:00 am - 9:50 am | **Registration / Introductory Remarks** | (NSC Room 222) |
| 10:00 am-10:50 am | **Keynote Presentation:** | (NSC Room 215) |

**Professor Ellen M. Matson, University of Rochester**

*Redox-active, Metal-oxide Clusters for Multielectron Transformations and Energy Storage*

| | | |
|---|---|---|
| 11:00 am - 1:00 pm | **Student Oral Presentations** | (NSC Room 215) |
| 1:00 pm - 2:00 pm | **Lunch** | (NSC Room 222) |
| 2:00 pm - 3:30 pm | **Student Poster Session** | (NSC Foyer) |
| 3:30 pm | **Symposium Awards and Closing remarks** | (NSC Room 215) |

University at Buffalo
The State University of New York
The Department of Chemistry

ACS of Western New York

## Oral Presentations

10:00 AM - 12:30 PM (NSC Room 215)

### Keynote Address

10:00 am **Ellen M. Matson** University of Rochester

*Redox-active, Metal-oxide Clusters for Multielectron Transformations and Energy Storage*

### Student Presentations

11:00 am - 11:20 am: **Roshaan Surendhran** University at Buffalo

*Deciphering the Mechanism of $O_2$ Reduction with Electronically Tunable Non-Heme Iron Enzyme Model Complexes*

11:20 am - 11:40 am: **Emily Steiner** Niagara University

*Studies Toward the Synthesis of ent-Artemisin, a Potential Anti-Malarial Compound*

11:40 am - 12:00 pm: **Merjema Purak** University of Rochester

*Kumada Coupling of Halogenated N-Heterocycles Using a Manganese Salt*

11:00 pm - 12:20 pm: **Anthony Berardi** Canisius College

*β-Cyclodextrin-Based Amphiphiles as Contrast Agents for $^{19}F$ Magnetic Resonance Imaging*

12:20 pm - 12:40 pm: **Elida Bani** York University

*TRESI HDX in Probing the Interaction of Alpha Synuclein as a Monomer and Oligomer with TREVENTIS Small Molecules and EGCG*

12:40 pm - 1:00 pm: **Justin T. Keck and Jake D. Urbano** Penn State Behrend

*Detection of Narcotics in Beverages Using Colorimetric Methods*

## Student Abstracts

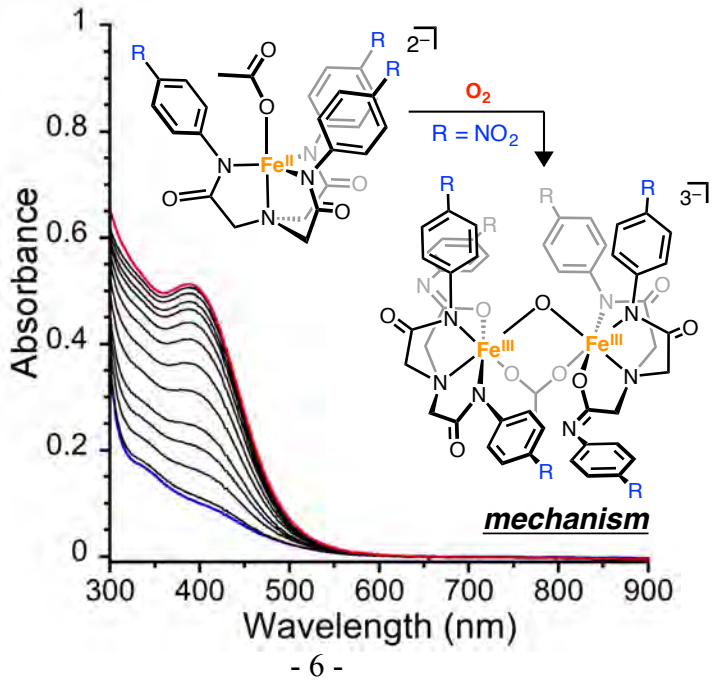
**Talk 1**

# Deciphering the Mechanism of $O_2$ Reduction with Electronically Tunable Non-Heme Iron Enzyme Model Complexes

***Roshaan Surendhran***[1], *Alexander A. D'Arpino*[1], *Bao Y. Sciscent*[1], *Anthony F. Cannella*[1], *Alan E. Friedman*[2], *Samantha N. MacMillan*[3], *Rupal Gupta*[4] *and David C. Lacy*[*,1]

[1]Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY
[2]Department of Materials Design & Innovation, University at Buffalo, SUNY, Buffalo, NY
[3]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
[4]Department of Chemistry, College of Staten Island, CUNY, Staten Island, NY

A homologous series of electronically tuned 2,2',2''-nitrilotris(N-arylacetamide) preligands ($H3L^R$) were prepared (R = $NO_2$, CN, $CF_3$, F, Cl, Br, Et, Me, H, OMe, $NMe_2$) and their corresponding metal (Mn, Fe, Co, Zn) species synthesized. The iron complexes react rapidly with $O_2$, the final products of which are diferric mu-oxo bridged species. The crystal structure of the oxidized product obtained from DMA solutions contain a structural motif found in some diiron proteins. The mechanism of iron mediated $O_2$ reduction was explored to the extent that allowed us to construct an empirically consistent rate law. Furthermore, the temperature dependence of the rate constant revealed an interesting negative enthalpy of activation. Finally, a Hammett plot was constructed that enabled insightful information into the rate-determining step and hence allow for a differentiation between two kinetically equivalent $O_2$ reduction mechanisms.



**Talk 2**

# Studies Toward the Synthesis of *ent*-Artemisin, a Potential Anti-Malarial Compound

***Emily Steiner**, Mary Hejna and Luis Sanchez**

Department of Biochemistry, Chemistry, and Physics, Niagara University, NY

Artemisinin is a natural product isolated from the plant *Artemisia annua* that is currently the fastest-acting treatment available against *Plasmodium falciparum*—the protozoan parasite that causes the deadliest form of malaria. The low bioavailability of this compound and its short half-life, however, make the cost of artemisinin therapies very high. Anti-malarial *combination* therapies involving artemisinin are employed to avoid the development of resistance to the drug by the parasite, as recommended by the World Health Organization.

Artemisinin's structure contains a unique peroxide bridge that is believed to be responsible for the drug's mechanism of action. We gather that the exceptional biological activity of this compound may originate in the fine-tuned chemical reactivity of its peroxide bridge, rather than the topology of the structure itself. Consequently, we hypothesize that its enantiomer (*ent*-artemisinin)—a yet unreported compound—could exhibit comparable anti-malarial properties. Seeking an affordable synthetic route, our current goal is to develop a reaction sequence to produce *ent*-artemisinin from zingiberene, a compound found in ginger oil. Thus far we have successfully isolated a ginger oil fraction in which zingiberene is the primary component (as per NMR analysis) and further purified it via a series of reactions. We have recently begun studies into the synthesis of the *ent*-artemisinin precursor molecule, *ent*-amorphadiene, from zingiberene, and have been analyzing this process via LCMS. If this proposed synthetic route is successful, we believe that the low cost and high availability of ginger oil would allow for the large-scale production of *ent*-artemisinin.

**Talk 3**

# Kumada Coupling of Halogenated N-Heterocycles Using a Manganese Salt

***Merjema Purak**, Brittney Petel and Ellen Matson**

Department of Chemistry, University of Rochester, Rochester, NY

Metal-mediated cross-coupling reactions have become one of the most synthetically applicable reactions for organic synthesis. While precious metal complexes have dominated as catalysts, recent years have seen an upswing in the use of first-row transition metals because of their abundance and low toxicity. This work presents the use of a simple manganese(II) salt as a catalyst for C-C bond formation between halogenated N-heteroaryl electrophiles and alkyl- and aryl-Grignard reagents. With ambient conditions (20-50°C) and short reaction times (15 minutes – 20 hours), high yields can be achieved of the desired cross-product, using only 3 mol % catalyst loading. Manganese was shown to tolerate varying electronic environments of the substrate, producing moderate to high yields of product with electron-donating or -withdrawing substituents.

**Talk 4**

# β-Cyclodextrin-Based Amphiphiles as Contrast Agents for $^{19}$F Magnetic Resonance Imaging (MRI)

***Anthony J. Berardi**, Samantha T. Caico, Lauryn E. Rudin and Jeremy L. Steinbacher**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

The move toward $^{19}$F-containing MRI contrast agents presents an exciting opportunity to improve upon MRI contrast agents used currently in the clinic. Biologically-occurring organofluorines are very rare, so when exogenous fluorine-containing molecules are administered to the body and imaged with $^{19}$F MRI, no background signal from natural sources is detected. Thus, $^{19}$F imaging agents can theoretically provide greater contrast than conventional MRI contrast agents. We have synthesized fluorine-containing silica nanoparticles that exhibit sufficient fluorine NMR signal to acquire spectra over short amounts of time. Recently, we have begun investigating β-cyclodextrin as a potential platform for a novel $^{19}$F imaging agent. β-cyclodextrin is a naturally-occurring, readily-available nanomaterial composed of seven glucose molecules arranged in a cone-like ring. The ring has a "primary face" with 14 exposed primary alcohols, a "secondary face" with seven exposed secondary alcohols, and a hydrophobic core. The difference in reactivity of each face, along with its hydrophobic core, allow for facile functional group manipulation and the formation of inclusion complexes with other hydrophobic molecules. Here, we report several synthetic approaches toward non-toxic, water-soluble, fluorinated amphiphiles based on β-cyclodextrin that can be micellized and used as $^{19}$F imaging agents.

**Talk 5**

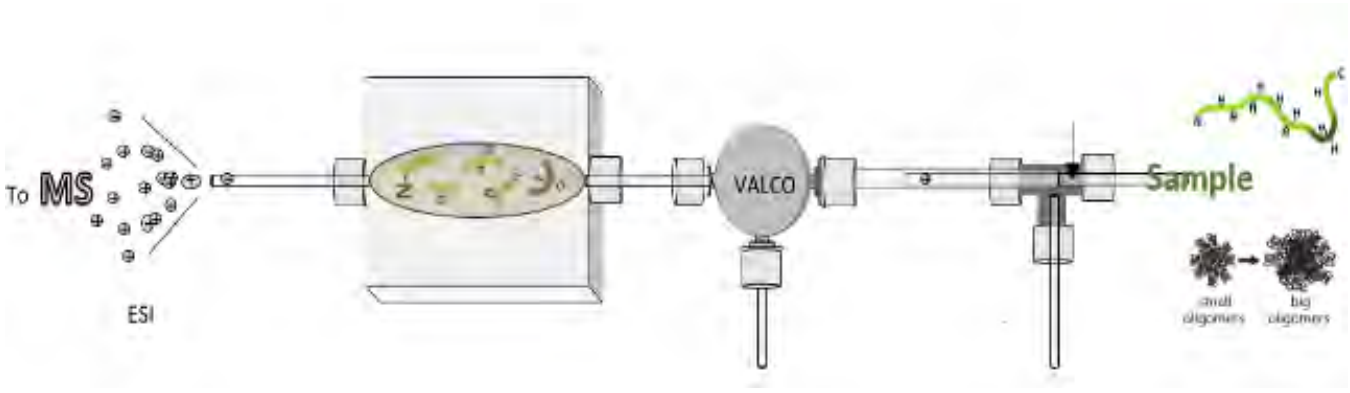
# TRESI HDX in Probing the Interaction of Alpha Synuclein as a Monomer and Oligomer with TREVENTIS Small Molecules and EGCG

***Elida Bani**, Shenbaga Moorthy and Derek Wilson**

Department of Chemistry, York University, Toronto, ON.

Alpha-synuclein, an intrinsically disordered protein, is associated with Parkinson's Disease (PD), and it tends to aggregate when overexpressed or mutated typically at the N-terminal domain. There is evidence that the aggregates are toxic to neurons. Thus, preventing monomers to aggregate or disaggregating oligomers, is a promising therapy to prevent PD from progressing. Here we demonstrate the use of time-resolved electrospray ionization hydrogen-deuterium exchange (TRESI-HDX) to probe the interaction of TREVENTIS small molecules, TRV001/ TRV002/ TRV003, and EGCG with alpha-synuclein as a monomer and an oligomer. TRESI-HDX technique employs an on-line microfluidic apparatus that enables millisecond HDX labeling times with a proteolytic chamber and electrospray ionization (ESI). The findings indicate that none of the TREVENTIS small molecules interact with monomeric or oligomeric alpha-synuclein. However, EGCG shows weak binding with monomeric α-Synuclein at N-terminal and NAC domain. In addition, EGCG shows significant protection in deuterium uptake in C-terminal domain of oligomeric alpha-synuclein, whereas, N-terminal and NAC domains of oligomeric alpha-synuclein show same level of deuterium uptake as monomers. Ultimately, binding of EGCG to C-terminal regions prevents α-Synuclein oligomer formation.

Keywords: α-Synuclein; TRESI HDX; Mass Spectrometer; Monomer; Oligomers; EGCG.



**Talk 6**

# Detection of Narcotics in Beverages Using Colorimetric Methods

***Justin T. Keck, Jake D. Urbano*** *and Luciana Aronne**

School of Science, Penn State Behrend, Erie, PA

The narrow research on the topic of date rape drugs is extremely alarming. The purpose of the research being conducted is to determine if certain compounds commonly known as "date rape drugs can be both tested for and detected via the use of a colorimetric method. The main goal for this research is to in future, develop a product to detect these date rape drugs. The product must be gender neutral, have the ability to test drinks on site, have a certain degree of inconspicuousness, and provide a quick result. It is believed that using a colorimetric method will increase the ease of use and simplicity for the consumers. The drugs are typically administered through the contamination of an alcoholic beverage unbeknownst to the victim. The best defense against this is prevention. If the drinks can be easily tested for contamination before consumption, then the threat generally decreases. This presentation will discuss the experimental methods developed on compounds similar to common date rape drugs to determine their presence in alcoholic or non-alcoholic beverages.

## Student Poster Presentations

Time: 2:00-3:30 PM (NSC Foyer)

**Poster 1.** **Abhilash Kavuru**, Cristina Lento, Derek J. Wilson* and David Josephy
*Department of Chemistry, York University, Toronto, ON*

Understanding Conformational Dynamics of Substrate Binding to GST M2-2 Using TRESI-HDX

**Poster 2.** **Arianna R. Rothfuss**, Tammy M. Milillo and Joseph A. Gardella, Jr.*
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

Modeling Historic Deposition from the Tonawanda Coke Corporation

**Poster 3.** **Eric Frauenhofer** and Jamie Kim*
*Department of Chemistry, SUNY Buffalo State College, Buffalo, NY*

Use of Inverse Gas Chromatography to Study the Absorption of Volatile Gasoline Residues to Common Household Materials for Potential Application in Forensic Science

**Poster 4.** **Connor Lynch**, Elliott Martin, Steele Burgeson and Luis Sanchez*
*Department of Biochemistry, Chemistry, and Physics, Niagara University, NY*

Development of a Biaryl Oxidative Coupling-Based Route to the Anti-Tumor Natural Products TMC-95

**Poster 5.** **Connor Gould, CeDrice B. Howard** and David T. R. Stewart*
*Department of Chemistry, D'Youville College, Buffalo, NY*

Work Towards the Use of Silicone Wristbands as Personal Passive Sampling Devices for Environmental Contaminants

**Poster 6.** **David M. Filion, Benjamin T. Russ** and Phillip M. Sheridan*
*Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY*

Laser Ablation/Molecular Jet Laser Excitation Spectroscopy of CaNCO

**Poster 7.** **Dong Kim**, Akansha Patel and Janet Morrow*
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

Selective Fluorescent Sensor for Iron (II) in the Biological Media

**Poster 8.** **Alexandra M. Izydorczak** and Scott Simpson*
*Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY*

Prediction of Polybrominated Diphenyl Ether Retention Times via Ab Initio Calculations

**Poster 9.** **Connor Chew**, Zachary Mariani, Stephanie Scharmach and Luis Sanchez*
*Department of Biochemistry, Chemistry, and Physics, Niagara University, NY*

Tuning Chemoselectivity Toward an Affordable Synthesis of Aurantioclavine

**Poster 10.** **Luke Izydorczak**, Eryn K. Matich, Berat Z. Haznedaroglu and G. Ekin Atilla Gokcumen*
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

LC-MS – Based Analysis of Phytosterols from an Oleaginous Green Microalgae

**Poster 11.** **Olivia Kim** and Christopher Patridge*
*Department of Chemistry, D'Youville College, Buffalo, NY*

Synthesis and Characterization of Candidate Materials for Multi-Valent Aqueous Rechargeable Batteries

**Poster 12.** **Benjamin T. Russ** and Phillip M. Sheridan*
*Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY*

Computational Study of Aluminum Monoisocyanate Isomers

**Poster 13.** **Ariel Burgio**, Eric Snyder and Janet Morrow*
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

Triazole Appended Macrocycles with Potential Applications in MRI Imagining

**Poster 14.** **Emilee R. Welton**, Julia L. Freemire and Robyn E. Goacher*
*Department of Biochemistry, Chemistry and Physics, Niagara University, NY*

Optimizing the 3,5-Dinitrosalicylic Acid (DNS) Assay for Glucose and Xylose in Varied Buffers

**Poster 15.** **Joshua Hazelnis**, Timothy Cook* and Anjula Kosswattaarachchi
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

The Molecular Chemistry Of Redox Flow Batteries

**Poster 16.** **Maham Alamgir**, Brent Boleslav and Dr. Robyn E. Goacher*
*Department of Biochemistry, Chemistry and Physics, Niagara University, NY*

Distributed Pharmaceutical Analysis Laboratory (DPAL): Metformin Analyzed via HPLC

**Poster 17.** **Catherine C. Lincourt**, Dhvani Patel, Peter Cao, Yasser Heakal* and Dominic L. Ventura*
*Department of Chemistry, D'Youville College, Buffalo, NY*

Synthesis and Evaluation of Chloroquine Analogs in Breast Cancer Cells

**Poster 18.** **Matthew Berardi, Filippo Gentile**, Isabelle Kozik and Timothy M. Gregg*
*Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY*

The Aldol Condensation Lab Experiment: Validation of Student Reaction Rate Observations

**Poster 19.** **LeAnn Richert** and Luis Sanchez*
*Department of Biochemistry, Chemistry, and Physics, Niagara University, NY*

A Shapiro Elimination/Epoxidation-Based Strategy for the Synthesis of Cage Molecule Building Blocks

**Poster 20.** **Christina White**, Jungeun Park, Zoe Vaughn, Lauren Lubecki and Joseph A. Gardella Jr.*
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

Studies of Water Content of HEMA (2-Hydroxyethyl Methacrylate) Hydrogels Via Swelling for Drug Delivery Applications

**Poster 21** **Sarah A. Gehl** and Robyn E. Goacher*
*Department of Biochemistry, Chemistry, and Physics, Niagara University, NY*

Ink Aging: Does Leaving Inks for One Week or One Month Alter Which Appears on Top?

**Poster 22.** **Samantha T. Caico**, Anthony J. Berardi, Lauryn E. Rudin and Jeremy L. Steinbacher*
*Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY*

Synthesis of Fluorinated Molecules for Functionalization of Porous Silica Nanoparticles for use as 19F NMR Contrast Agents

**Poster 23.** **Alexander A. D'Arpino**, Roshaan Surendhran, Bao Y. Sciscient, Anthony F. Cannella, Alan E. Friedman, Samantha N. MacMillan, Rupal Gupta and David C. Lacy*
*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

Probing Non-Heme Enzyme Active Sites with Tunable Ligand Scaffolds

**Poster 24.** **Zachary J. Augustyn** and Robyn E. Goacher*
*Department of Biochemistry, Chemistry, and Physics, Niagara University, NY*

Synergy Between Simultaneous and Sequentially Applied Laccase and Xylanase in the Degradation of Wood into Biofuels

## Student Abstracts

**Poster 1**

# Understanding Conformational Dynamics of Substrate Binding to GST M2-2 Using TRESI-HDX

***Abhilash Kavuru***[1]*, Cristina Lento*[1]*, Derek J. Wilson*[1]** and David Josephy*[2]

Department of Chemistry, York University, Toronto, ON[1]
Department of Molecular and Celluar Biology, University of Guelph, Guelph, ON[2]

Protein dynamics is very important to understand the proper functioning and utility of enzymes. Hydrogen-Deuterium exchange (HDX) experiments coupled with mass spectrometry allow for a unique visualization of the structural changes during protein-ligand interactions. The transition between enzymatic states can be studied before equilibrium is established by using continuous flow, time-resolved electrospray ionization (TRESI) with a subsecond HDX reaction quenched by continuous flow acid and coupled directly to the mass spectrometer. GST M2-2 was analyzed using TRESI-HDX mass spectrometry and it was determined that when glutathione (GSH) bound the G-site, the site and surrounding protein scaffolding became less dynamic and more structured. This holds the substrate in the binding pocket preventing easy diffusion into the environment and effectively increases affinity of enzyme to the substrate. When CDNB, 2,4-dinitrochlorobenzene, bound to the H-site, the surrounding structure did not show any significant reaction which explains the non-specific nature and a broad spectrum of substrate binding to the H-site. In both conditions a significant transformation was noticed in the empty binding site as they became more dynamic indicating the enzyme is more receptive to binding the second substrate once the first substrate has bound, regardless of the order.

**Poster 2**

# Modeling Historic Deposition from the Tonawanda Coke Corporation

***Arianna R. Rothfuss**, Tammy M. Milillo and Joseph A. Gardella, Jr.**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

The Tonawanda Coke Corporation currently manufactures coke, a fuel with a high carbon content, for steel production which creates byproducts of elemental sulfur, ammonium sulfate, benzene, toluene, xylene, and naphthalene. Geographic information analysis (GIA) has a variety of techniques that can be applied to characterize and/or determine the legacy pollution that impacts communities and the environment. Phase one of this study has resulted in the collection of 185 soil sample points which have shown historic soil deposition thought to stem from Tonawanda Coke Corporation. By analyzing for polychlorinated biphenyls (PCBs), pesticides, semi-volatile organic compounds (SVOCs), and volatile organic compounds (VOCs), geostatistical modeling techniques can be applied to visualize the impact of contamination on the surrounding neighborhood. Maps were created showing the contaminant distributions and hot spots, or regions of interest, were able to be determined. These hot spots will later be resampled in the second phase of sampling to track how the contaminants migrate over time and to obtain a better understanding of the boundaries of the contaminated area.

**Poster 3**

# Use of Inverse Gas Chromatography to Study the Absorption of Volatile Gasoline Residues to Common Household Materials for Potential Application in Forensic Science

***Eric Frauenhofer*** *and Jamie Kim**

Department of Chemistry, SUNY Buffalo State College, Buffalo, NY

Investigation of volatile/semi-volatile organic compounds such as gasoline residues adsorbed on solid substrates is an important subject in many areas of science including forensics and environmental science. For example, detection and identification of gasoline residues present in solid substrates is one of the key issues in fire investigation. Headspace concentration method coupled with solid phase microextraction (HS-SPME) is a popular method for detecting volatile organic compounds from solid samples. However, the compositions of volatile compounds analyzed via HS-SPME are generally different from the true compositions because the partition coefficients of volatile compounds at the air/solid interface are not equal. Our current research focuses on the investigation of adsorption properties of volatile hydrocarbons existing in gasoline residues to household materials via inverse gas chromatography. Thermodynamic data and partition coefficients obtained from this project will be used for quantitative chemical analysis of these compounds adsorbed on solid substrates via HS-SPME. For this project, inverse gas chromatographic measurements of selected hydrocarbons (*n*-heptane, *n*-octane, *n*-nonane, *n*-decane, toluene, *p*-xylene, and *1,2,4*-trimethylbenzene) using columns packed with cardboard, cotton fabric, and carpet were conducted in the temperature range of 40 - 90 °C. Estimated free energies and enthalpies of adsorption, sorption isotherm, and partition coefficients of these hydrocarbons on solid substrates will be presented.

**Poster 4**

# Development of a Biaryl Oxidative Coupling-Based Route to the Anti-Tumor Natural Products TMC-95

***Connor Lynch**, Elliott Martin, Steele Burgeson and Luis Sanchez**

Department of Biochemistry, Chemistry, and Physics, Niagara University, NY

First isolated from the fermentation broth of *Apiospora montagnei* Sacc. TC 1093, the natural products TMC-95 A–D are of great interest because of their biological activity against the 20S proteasome. This distinctive activity makes them promising candidates as agents for the treatment of cancer. However, constructing such complex molecular structures requires many synthetic steps, which hinders their potential medical use. These active compounds feature a peptide-based structure composed of tyrosine, asparagine, a highly oxidized tryptophan, (*Z*)-1-propenylamine, and 3-methyl-2-oxopentanoic units. A particularly unusual bond is found in these natural products: a biaryl connection between the tryptophan and tyrosine residues and, as a result of this strange C–C linkage, axial chirality is observed around this bond. Our primary interest in this project is to develop chemical conditions to form this important biaryl linkage via oxidative coupling of suitable tripeptide-based building blocks. Such an oxidative coupling can make the synthetic production of TMC-95 significantly easier, by starting with the inexpensive and widely available natural amino acid units. With an easier synthetic route, TMC-95-based compounds could become viable anti-tumor drug candidates.

**Poster 5**

# Work Towards the Use of Silicone Wristbands as Personal Passive Sampling Devices for Environmental Contaminants

***Connor Gould, CeDrice B. Howard*** *and David T. R. Stewart**

Department of Chemistry, D'Youville College, Buffalo, NY

Silicone wrist bands (SWB) can be used to detect personal exposure to harmful chemicals present in the environment. They are efficient at collecting a wide range of nonpolar organic compounds [1]. Silicone wristbands are an easy and affordable method of collecting data without interrupting the daily activities of the wearers. A completed method would consist of three general steps: 1) a human subject would wear the SWB for a defined period, 2) the chemicals absorbed by the SWB would be extracted into a liquid solvent, 3) the solvent would be analyzed by gas chromatography mass spectrometry (GCMS) for quantitative analysis. The detected chemicals and the relative amounts and concentrations found may correlate to various socio-demographic differences.

The chemicals selected for this initial process include toluene, oxybenzone, chlorobenzene, and N,N-diethyl-meta-toluamide (DEET). GCMS can separate and qualitativly determine the presence of the target compounds from an extraction. External calibration curves that will allow the concentrations of the target compounds to be determined are currently under development. The current chromatographic method can accommodate future compounds without extensive modification. Future work will include the development of a method for extracting the target compounds from silicon wristbands with consistent yields.

The portion of the project presented currently is work towards objective number 1.

[1] Kile, M. L.; Scott, R. P.; O'Connell, S. G.; Lipscomb, S.; MacDonald, M.; McClelland, M.; Anderson, K. A. Using Silicone Wristbands to Evaluate Preschool Children's Exposure to Flame Retardants. *Environmental Research* **2016**, *147*, 365-372.

**Poster 6**

# Laser Ablation/Molecular Jet Laser Excitation Spectroscopy of CaNCO

***David M. Filion, Benjamin T. Russ*** *and Phillip M. Sheridan**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

Metal monoisocyanates (MNCO) are the simplest molecules containing a metal atom bonded to carbon, nitrogen, and oxygen. Unfortunately, few have been investigated either experimentally or computationally. Experimentally, CaNCO has been the subject of a single study: low-resolution laser excitation spectroscopy using a Broida-type oven for molecular synthesis. This work suggested that CaNCO is linear in its ground and lowest excited electronic states, however, this could not be confirmed. In addition, there is uncertainty as to whether the lowest energy isomer has the metal bonded to nitrogen (CaNCO) or to oxygen (CaOCN). To further investigate these fundamental structure and bonding questions we have initiated a study of CaNCO using our laser ablation/molecule jet spectrometer system. No metal monoisocyanate has been previously synthesized in the gas phase using laser ablation. We have successfully produced CaNCO by this method using HNCO as the reactant gas. The resulting low-resolution laser excitation spectra of the A – X and B – X transitions exhibit a much narrower appearance than the Broida-oven work due to the significantly lower rotational temperature of the molecules in the jet. Our next step will be to record rotationally resolved spectra of the A – X and B – X transitions using high-resolution laser excitation spectroscopy.

**Poster 7**

# Selective Fluorescent Sensor for Iron (II) in the Biological Media

***Dong Kim**, Akansha Patel and Janet Morrow**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Iron is an essential metal ion for the active site of proteins in the body, which are involved in oxygen transport, cellular respiration, energy metabolism, immune function and neurotransmitter production in the brain. On the other hand, malfunction of iron regulatory pathways in the body can lead to cellular damage with iron overload, which are 'free iron ions' that are unbound to proteins in cells. There is an increasing interest in studying diseases associated with iron overload in cells such as hemochromatosis and neurodegenerative diseases. However, due to our limited understanding of redox activity of free iron ions in cells and cellular ligands, free iron ions are challenging metals to study.

In our group, we are working towards developing a fluorescent sensor for detection of iron (II). Our design includes a metal selective recognition site for iron (II) binding and is linked with a fluorescent signaling unit. This probe has advantages of high sensitivity and water solubility, and is non-toxic in a cellular environment. The metal binding leads to an increase in fluorescence response hence indicating binding event. Preliminary results show promising selectivity towards iron (II) in cells.

**Poster 8**

# Prediction of Polybrominated Diphenyl Ether Retention Times via Ab Initio Calculations

***Alexandra M. Izydorczak*** *and Scott Simpson**

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The goal of this study is to use density functional theory calculations paired with experimental gas chromatographic retention times in order to predict the identity of unknown polybrominated diphenyl ethers (PBDEs) congeners. This was accomplished by calculating different structural parameters of the ground state geometry of a number of PBDEs, which are toxic bio-accumulative persistent compounds. GAMESS was used to calculate the ground lowest energy structure of PBDEs. In order to identify these unknown congeners, we determined a relationship with experimentally determined retention times from gas chromatography and C-O bond length, C-O-O bond angle, C-C-O-C dihedral angle, bond order, and dipole moment of the PBDEs.

**Poster 9**

# Tuning Chemoselectivity Toward an Affordable Synthesis of Aurantioclavine

***Connor Chew**, Zachary Mariani, Stephanie Scharmach and Luis Sanchez**

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Aurantioclavine is a natural product isolated from *Penicillium aurantiovirens* that gained the interest of the synthetic community for its proposed role in the biosynthesis of the complex polycylic alkaloids of the communesin family. Members of this family display notable bioactivities, including insecticidal properties and cytotoxicity toward leukemia cell lines.

Our interest in this important compound lies in its structural resemblance to tryptamine, a derivative of the amino acid tryptophan. Since tryptamine is readily available and more than a hundred times less expensive than the starting materials used in the reported total syntheses of aurantioclavine, we aim at developing a rational reaction sequence to progressively transform tryptamine and access aurantioclavine synthetically. This approach, nevertheless, is bound to involve an "unfavored" cyclization in order to assemble aurantioclavine's characteristic seven-membered ring. We expect to tune the chemical selectivity of this process via the functionalization of the indole ring and pendant chain of tryptamine—altering the geometry and electronics of the functionalities involved in the cyclization. Our progress in these efforts will be presented.

**Poster 10**

# LC-MS – Based Analysis of Phytosterols from an Oleaginous Green Microalgae

***Luke Izydorczak***[1]*, Eryn K. Matich*[1]*, Berat Z. Haznedaroglu*[2] *and G. Ekin Atilla Gokcumen**[1]

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[2] Institute of Environmental Sciences, Bogazici University, Istanbul, Turkey

Green microalgae utilize $CO_2$ in the atmosphere during growth while producing value added bio-products. Microalgae are even more advantageous than terrestrial plants in this regard because they can remove $CO_2$ from the atmosphere more efficiently due to their rapid growth. Unfortunately, obtaining value added bio-products directly from microalgae is not yet competitive due to the limited production capacity of these organisms. Phytosterols produced by green oleaginous microalgae are important nutraceuticals; they can be precursors for vitamins, or when ingested directly, have other health benefits. Previous research has aimed to identify nutrient conditions during growth under which the production of value added bio-products by the algae are maximal. In the previous lipidomic study on the green oleaginous microalgae species *Ettlia oleoabundans* conducted in the Atilla laboratory, phytosterols did not ionize well via electrospray ionization. Therefore, the current research aim is to develop a method to improve detection of the phytosterols. It was determined that a method that will improve the ionization efficiency significantly was required since solid phase extraction efforts did not yield any improvement on detection limits. Three derivatization methods to modify the 3-hydyroxyl groups of phytosterols with readily ionizable groups were tested. Dimethylglycine modification was determined to be most efficient method based on complete derivatization of a standard solution of a sterol mixture. The application of this method to extracts grown under various growth conditions to investigate the levels of different phytosterols, are underway.

**Poster 11**

# Synthesis and Characterization of Candidate Materials for Multi-Valent Aqueous Rechargeable Batteries

***Olivia Kim*** *and Christopher Patridge**

Department of Chemistry, D'Youville College, Buffalo, NY

The search and reevaluation of materials for batteries that could meet the rising demands on portable energy needs has expanded beyond the well-known Li-ion batteries. While this system (Li-ion) has been well studied and at present is ubiquitous, it suffers from abrupt thermal runaway (fires/explosions) and relatively high cost for the raw materials (Li metal, organic solvents). Lesser known materials and systems have slowly emerged as alternative battery chemistries that have some distinct advantages over Li-ion. The use of a different ion such as $Zn^{+}$, $Mg^{2+}$, or $Al^{3+}$ allows increased electricity (more energy) because these ions carry more charge than Lithium and have been shown to facilitate metallic anode viability (Zn). Coupling this approach with vanadium oxides, which possesses rich structure of either very large open tunnels and/or alternate open layers ideal for intercalation of ions, and there is a large parameter space to search for candidate materials.

We have tested various conditions using hydrothermal methods to synthesize nanostructured materials with evidenced approximate stoichiometry of $Zn_{0.4}V_2O_5 \bullet zH_2O$. We have collected information on the structure, nanostructured morphology, and the atomic ratios between elements in the material. Work is ongoing to characterize the materials' electrochemical properties and solidify the precise crystalline structure for our material.

**Poster 12**

# Computational Study of Aluminum Monoisocyanate Isomers

***Benjamin T. Russ*** *and Phillip M. Sheridan**

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Metal monoisocyanates (MNCO) and their isomers are the simplest metal molecules containing nitrogen, carbon, and oxygen. These species are of fundamental interest because six M-ligand isomers (linear and bent geometries) are possible (more if metal insertion products are considered.) However, unlike metal monocyanides and monohalides, experimental and computational studies of metal monoisocyanate species are extremely limited. Therefore, we have initiated a computational study of the isomers of aluminum monisocyanate. Using DFT and CCSD methods, we have calculated the energies of the linear and bent M-ligand isomers as well as several metal insertion products. For both methods, linear AlNCO was found to be the lowest energy isomer. Relative energies of the other isomers, geometric parameters, vibrational frequencies, dipole moments, QTAIM charges, and other molecular properties have been calculated. Rotational constants determined in this study will assist eventual experimental microwave spectroscopic studies of AlNCO.

**Poster 13**

# Triazole Appended Macrocycles with Potential Applications in MRI Imagining

***Ariel Burgio**, Eric Snyder and Janet Morrow**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Magnetic resonance imaging (MRI) is used in the medical field for diagnosis and prognosis for diseases. MRI has high spatial resolution and soft tissue contrast which makes it ideal for evaluating the treatment of solid tumors. However, MRI has poor sensitivity so contrast agents need to be used to enhance the quality of MRI images. Currently the FDA approved contrast agents utilize gadolinium due to their ideal magnetic properties. However, there has been increasing evidence of toxicity associated with gadolinium release in the body. We propose a safer alternative to gadolinium contrast agents that utilize iron(III). We utilize macrocyclic complexes because we can optimize and functionalize properties for MRI imaging. Different pendants on these macrocycles can potentially change solubility, coordination and the distribution of the MRI contrast agent in the body. In this project we have synthesized a triazole donating group on a TACN macrocycle using click chemistry. Click chemistry allows the rapid construction of triazole compounds through a highly selective and efficient reaction between an alkyne and azide. Furthermore, copper catalyzed (CuAAC) click chemistry allows us to control the regioselectivity of the reaction. Click chemistry is also attractive because triazoles have favorable solubility properties and are resistant to metabolic degradation. We have synthesized two triazole appended macrocyclic iron complexes. Preliminary data from these complexes is promising for their development as alternatives to gadolinium contrast agents.

**Poster 14**

# Optimizing the 3,5-Dinitrosalicylic Acid (DNS) Assay for Glucose and Xylose in Varied Buffers

***Emilee R. Welton**, Julia L. Freemire and Robyn E. Goacher**

Department of Biochemistry, Chemistry and Physics, Niagara University, NY

Biofuel production from lignocellulose relies on the release of simple sugars such as glucose and xylose, as the result of the degradation of polysaccharides in wood. Measurement of sugars in solution is often done by the DNS colorimetric assay. Glucose and other sugars cannot be measured directly by UV-VIS spectroscopy because they do not absorb light in this range. However, previous researchers have shown that the nitro group on the DNS molecule is reduced in the presence of reducing sugars (like D-glucose) to form an amine group, producing the strongly colored 3-amino-5-nitrosalicylic acid. DNS is normally used in combination with a sodium acetate buffer or citrate buffer, but some enzyme treatments for wood degradation are done in other buffers. Both acetate and citrate buffers are monoprotic, meaning they have a smaller pH range and buffer capacity. Universal buffer, containing phosphoric acid, acetic acid, and boric acid, is a polyprotic buffer, meaning it has a larger pH range and much larger buffer capacity, making the traditional method of DNS insufficient with universal buffer. As a result, a new method for using the DNS assay in a universal buffer was designed, optimized and carried out for glucose and xylose.

**Poster 15**

# The Molecular Chemistry Of Redox Flow Batteries

***Joshua Hazelnis**, Timothy Cook* and Anjula Kosswattaarachchi*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Redox Flow Batteries (RFBs), which are identified as efficient large scale electrochemical energy storage devices, can be a solution for the unpredictable nature associated with renewable energy sources. In a flow battery there are electrolyte solutions pumped out of external reservoirs to go over the cell phase of electrodes, which are in the main cell component. In the main cell, there are two compartments separating the positive and negative solutions. In order to avoid mixing of the two solution sides, there is an ion exchange membrane. The resistance of the ion exchange membrane plays a critical role in the overall cell voltage that can be obtained by the device. Usually the membrane can display different resistance after being pre-treated under various conditions. In light of determining the range of commonly used membranes, we have used electrochemical impedance spectroscopy to map out and determine resistance values over time.

**Poster 16**

# Distributed Pharmaceutical Analysis Laboratory (DPAL): Metformin Analyzed via HPLC

***Maham Alamgir**, Brent Boleslav and Dr. Robyn E. Goacher**

Department of Biochemistry, Chemistry and Physics, Niagara University, NY

The Distributed Pharmaceutical Analysis Laboratory (DPAL)* is a project focused on the analysis of drugs in Africa, to identify mis-labeled or mis-dosed pills. Metformin is a pharmaceutical that is widely taken by individuals with Type-II diabetes. At Niagara University, we have worked to validate an HPLC method to determine whether metformin pills are indeed metformin, if they are dosed correctly, and whether there may be degraded products in the metformin. Our HPLC method is based on USP procedures for metformin analysis, adding a gradient column washing step. After this method passed system suitability checks and was approved by the DPAL project, the authors and analytical lab students at Niagara University analyzed 50 metformin tablets from Kenya against a calibration curve. Of these, 48 were found to be within 10% error of the labeled dosages. The remaining two pills were determined to be other pharmaceuticals in their corresponding packaging, which had been mixed into the metformin samples at some point between purchase and analysis. We are currently studying the stability of standard metformin solutions when stored at room temperature, and in the refrigerator (4°C) and freezer (-80°C). We are also working on separating additional metformin related compounds (MRCs) from Metformin via HPLC, and on quantifying these MRCs. It is hoped that the stability evaluation and MRC study will streamline and expand the utility of our HPLC analysis of metformin pills in the future.

* The DPAL Project is run by the University of Notre Dame. For more information, see http://padproject.nd.edu/get-involved/distributed-pharmaceutical-analysis-lab/

**Poster 17**

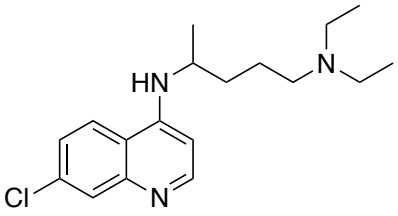
# Synthesis and Evaluation of Chloroquine Analogs in Breast Cancer Cells

***Catherine C. Lincourt***[1]*, Dhvani Patel*[1,2]*, Peter Cao*[2]*, Yasser Heakal*[2]** and Dominic L. Ventura*[1]***

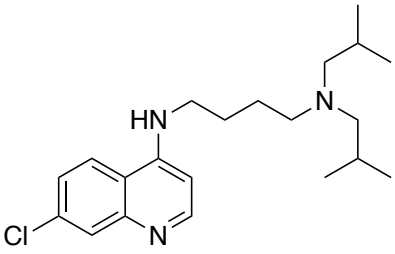
[1]Department of Chemistry, D'Youville College, Buffalo, NY
[2]Department of Pharmaceutical Sciences, D'Youville College, Buffalo, NY

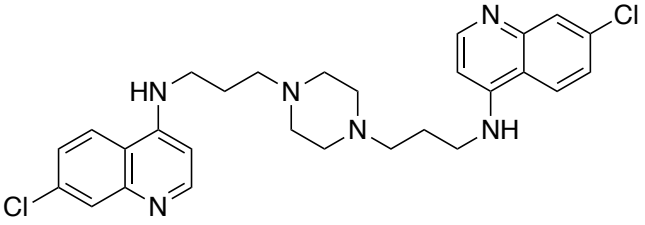
Chloroquine (CQ) is a chemotherapeutic agent and was also the foremost treatment of malaria for many years. More recently, Chloroquine has recently been investigated in the pharmacological inhibition of autophagy, although in high concentrations. Potentially, chloroquine derivatives may inhibit autophagy of breast cancer cells in much lower concentrations. In this study, we aimed to design and synthesize a group of CQ analogs through various methods. Utilizing various amines, we were able to produce a small library of compounds for this study (some examples shown below).

Once synthesized, the CQ analogs were tested for inhibition of autophagy in triple-negative breast cancer cells. This part of the project focused on taking advantage of polyamine transporters in targeting and delivering CQ, intracellularly.




Chloroquine (CQ)



**Poster 18**

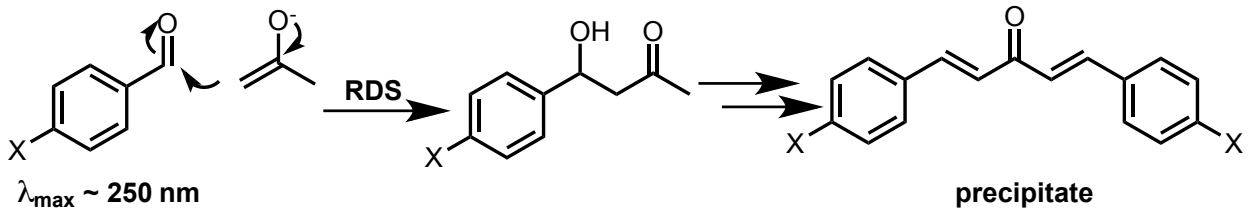
# The Aldol Condensation Lab Experiment: Validation of Student Reaction Rate Observations

***Matthew Berardi, Filippo Gentile**, Isabelle Kozik and Timothy M. Gregg**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

The Aldol Condensation is an important synthesis reaction between ketone and aldehyde reactants. Aldol chemistry has been highlighted in research literature, and at least 16 papers in *The Journal of Chemical Education* describe undergraduate lab experiments involving the aldol reaction. We are developing an aldol experiment for the Organic Chemistry sequence that highlights what students know about structural effects of different functional groups, and helps them observe their effects as they are manifested in aldol reactions that proceed at fast or slow rates in class.

We describe detailed reaction rate studies using UV absorption that allow us to follow the disappearance of benzaldehyde derivatives in the rate-determining aldol addition step. The Hammett correlation from this is nearly identical to a rough rate estimate using student observations of precipitate formation. Although not strictly identical to the rate-limiting addition of enolate nucleophile to aldehyde electrophile, precipitate formation is, nonetheless a fast, easy surrogate observation that allows students to see how substituent effects influence the rate-limiting step of the Aldol reaction.




**Cognate observations of reaction rate**

**Poster 19**

# A Shapiro Elimination/Epoxidation-Based Strategy for the Synthesis of Cage Molecule Building Blocks

***LeAnn Richert*** *and Luis Sanchez**

Department of Biochemistry, Chemistry, and Physics, Niagara University, NY

Platonic hydrocarbons and highly symmetric cage molecules have attracted the attention of chemists for decades. The first total synthesis of dodecahedrane, the simplest hydrocarbon with full icosahedral symmetry, more than thirty years ago was a remarkable and notorious achievement in organic chemistry. Still to date, however, the preparation of such compounds involves lengthy processes. Exploiting the elements of symmetry of the target cage molecules, as a tactic to minimize the necessary synthetic steps, is especially desirable.

We noticed that building blocks containing fused five-membered rings have been the central theme of a number of studies related to cage molecules. The idea of synthesizing symmetric compounds using polycyclizations, cycloadditions, and domino reactions continues to appear, even in very recent reports, but the preparation of the required substrates for such transformations has been generally unsuccessful. The present project offers both an alternative strategy and a method for the synthesis of $C_2$-symmetric cage molecule building blocks, which is based on a Shapiro reaction, an *m*CPBA-promoted epoxidation, and a β-elimination executed in sequence. Our approach and progress will be presented.

**Poster 20**

# Studies of Water Content of HEMA (2-Hydroxyethyl Methacrylate) Hydrogels Via Swelling for Drug Delivery Applications

***Christina White**, Jungeun Park, Zoe Vaughn, Lauren Lubecki and Joseph A. Gardella Jr.**

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Hydrogels based on 2-Hydroxyethyl methacrylate (HEMA) are an excellent model system as a drug delivery membrane. In our laboratory we are focused on loading hydrogels with Keratinocyte Growth Factor (KGF) protein for delivery to wounds in order to aid in the re-epithelialization process. Hydrogels' high water content, flexibility, biocompatibility, and ability to simulate natural living tissue make them ideal candidates for drug uptake and delivery. In order for a hydrogel to be considered suitable for therapeutic applications, it must be able to absorb a sufficient amount of the desired protein to aid in wound healing. An experiment was carried out, in which HEMA, a hydrophobic nonionic monomer unit, was reacted with several concentrations of the cross-linker trimethylolpropane trimethacrylate (TMPTMA) to produce hydrogels with different pore sizes. As the percentage of the cross-linker used decreases, pore sizes in the gels increase, which allows for greater water retention. Of the different formulations of HEMA hydrogels produced, the hydrogel with the lowest concentration of TMPTMA (0.1%) was considered the most favorable since its larger pore sizes allowed for greater water retention. With the intent of eventual KGF loading in the hydrogels, it is hypothesized that if water content increases as cross-linker density decreases, uptake of KGF protein will also follow this trend.

**Poster 21**

# Ink Aging: Does Leaving Inks for One Week or One Month Alter Which Appears on Top?

***Sarah A. Gehl*** *and Robyn E. Goacher**

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Ink forensics, and the ability to detect deposition order of inks can play an important role in the judicial and criminal justice systems. Determining the deposition order of inks would allow a forensic analyst to assess whether or not an important paper document had been forged or altered after the initial writing was completed. This research aims to continue exploring the use of Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), a surface sensitive technique, to analyze black ballpoint ink intersections, specifically Papermate, Bic and Staples brand pens.[1] Multiple data analysis techniques were used to determine the deposition order of the inks including Multivariate curve resolution (MCR) and regions of interest (ROIs). Previous work evaluated drying times of 1 minute, hour and day while this work explores samples that had 1 week and 1 month pass between writing the first and second lines. These samples were analyzed initially after the 2$^{nd}$ line was written, and again after three months. This project explores how the drying time influences the ability of ToF-SIMS to distinguish the inks and correctly portray the deposition order. Furthermore, inks were compared to see if there were any ink components that changed between the initial analysis and after months of aging.

1. Goacher, R. E.; DiFonzo, L. G.; Lesko, K. C., Challenges Determining the Correct Deposition Order of Different Intersecting Black Inks by Time-of-Flight Secondary Ion Mass Spectrometry. *Analytical Chemistry* **2017,** *89* (1), 759-766.

**Poster 22**

# Synthesis of Fluorinated Molecules for Functionalization of Porous Silica Nanoparticles for use as $^{19}$F NMR Contrast Agents

***Samantha T. Caico**, Anthony J. Berardi, Lauryn E. Rudin and Jeremy L. Steinbacher**

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Fluorine-containing magnetic-resonance imaging (MRI) contrast agents present an exciting opportunity to improve upon MRI contrast agents used currently in the clinic. We use porous silica nanoparticles (NPs) as a platform material that should enable combined MRI and drug delivery. NPs may be engineered to accumulate preferentially in tumors. Then, fluorine atoms immobilized to the pores may be imaged by $^{19}$F MRI while therapeutics in the pores release into the tumor, which decreases toxic exposure to healthy cells. We have synthesized fluorine-containing, porous silica NPs that exhibit sufficient fluorine NMR signal to acquire spectra over short amounts of time. Stimuli-responsive linkers are a type of fluorinated molecule that hold additional promise for targeted imaging. Depending on the solution conditions, the linker can selectively cleave, resulting in a "switch-on" response by $^{19}$F MRI, and therefore imaging specifically the area of concern. Tumors are generally acidic, and acyl hydrazones cleave under acidic conditions. Therefore, we pursued the synthesis of a fluorinated acyl hydrazone linker. Also, we have investigated a disulfide-containing linker that cleaves under reducing conditions, found in the interiors of cells. Our goal is to attach these linkers to silica nanoparticles and demonstrate a switch-on signal in $^{19}$F NMR in response to these stimuli.

**Poster 23**

# Probing Non-Heme Enzyme Active Sites with Tunable Ligand Scaffolds

***Alexander A. D'Arpino[1],*** *Roshaan Surendhran[1], Bao Y. Sciscient[1], Anthony F. Cannella[1], Alan E. Friedman[2], Samantha N. MacMillan[3], Rupal Gupta[4] and David C. Lacy*[1]*

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Oxygen reduction is one of the most prevalent processes in biology. It has become a heavily researched topic due to its potential for widespread application. Its importance influences everything from energy storage to biological activity. Enzymes play a key role in many pathways for oxygen reduction, and in order to gain insights to the reduction mechanism a great deal of attention has been given to the active sites of these enzymes. Iron centers in particular have shown to be common in these enzymes and appear in one of two types: heme and non-heme. Heme active sites are characterized by an iron coordinated to a porphyrin structure, while non-heme active sites lack the porphrynic coordination. While an enzyme may be capable of performing oxygen reduction, conducting mechanistic studies are difficult due to the nature of the active site. Implementing variations in the coordination or electronic environment within both heme and non-heme enzymes is essentially impossible; even with site-directed mutagenesis, the changes may lead to inactivity. Therefore, the development of biomimetic ligand systems offers a potential step toward illuminating the mechanisms, especially in non-heme systems. These ligands provide the ability to easily tune the electronic environment of an iron "center" via simple synthetic variations while still designing scaffolds that contain biologically relevant motifs. By synthesizing a ligand scaffold with systematic variations to the electronic substituents, a kinetic study can be conducted by developing a linear free energy relationship in order to investigate the potential oxygen reduction mechanisms.

**Poster 24**

# Synergy Between Simultaneous and Sequentially Applied Laccase and Xylanase in the Degradation of Wood into Biofuels

***Zachary J. Augustyn*** *and Robyn E. Goacher**

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With the ever-growing shortage of gasoline in today's modern industry, finding a fuel substitute is becoming increasingly important. A new field of research has opened with the interest of using plant-based materials as a new source of energy, in the form of cellulosic biofuels derived from wood. Polysaccharides in wood can be degraded into sugars, which can then be fermented into alcohol to be used as a fuel. A key portion of this research is to break down the lignin that sheaths the cellulose and hemicellulose (the polysaccharides). This poster will discuss a study of the synergy between two particular enzymes – laccase (which degrades lignin) and xylanase (which degrades the hemicellulose termed xylan). Specifically, the aspect studies how well the enzymes work together in the degradation process. This poster will show the relevant data for the analysis of enzyme-treated solid wood using several solid-sampling instruments (FTIR-ATR, TGA, and ToF-SIMS). The data were analyzed using principal component analysis (PCA) to identify trends in the treatments. This research has the potential to clarify one piece of the complex puzzle that is today's modern energy crisis.

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