Research Project Title: Functionalized ortho-carborane as a metal ion chelator

Student Presenter: Julia Berry

Faculty Mentor: Noel Paul

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Modern medicine frequently relies on magnetic resonance imaging (MRI), and the administration of chelated metal ions as contrast agents is often required to obtain sharp images. However, inevitable deposition of the toxic metal into the body imparts a low level of toxicity. Carboranes, which can possess the ability to bind metal ions, are of interest for their potential application in improvement of current macrocyclic contrast agents. The goal of this study is to develop a stable, carborane-based macrocycle with the capacity to chelate gadolinium ions and be developed into a viable MRI contrast agent. Initial work explored the cyclization of bis(butenyl)carborane via olefin metathesis, but the products exhibited especially low solubility, greatly complicating their purification and further analysis. Thus, studies that explore the feasibility of hydroxy-substituted carborane macrocycles in this hypothesis have been conducted. The reactivity of the ortho-carborane mono- and dianion have been examined in nucleophilic addition to various carbonyl compounds according to literature guidelines, and the products of these reactions were characterized using 1H and 13C NMR, and mass spectrometry. These methods have been considered as a means to introduce hydroxyl groups that may be used to coordinate gadolinium ions or serve as a handle to allow for cyclization. Current studies are expanding on this reactivity and exploring the use of dialdehyde molecules as potential routes to cyclization. Successful development of strong chelating agents would have a significant impact on medical imaging by minimizing deposition of toxic metal into the body, thereby reducing the risk associated with current MRI contrast agents.
Research Project Title: Binding affinities of functional groups to metal cations

Student Presenter: Michelle Fiamingo

Faculty Mentor: Heather Allen

Faculty Mentor Department: Chemistry

Research Abstract: Deciphering cation binding affinities for lipid head groups is essential in understanding the physical underpinnings of trace metal enrichment at the sea-surface microlayer (SSML). These metals and lipids at the SSML are incorporated into sea spray aerosols (SSAs) which in turn impact the climate through a myriad of direct and indirect methods. Surface tension experiments using salt titrations and surface pressure-area isotherms were conducted to probe metal binding to several model lipids, chosen for their high surface activities and varying headgroup moieties. In addition, Brewster Angle Microscopy (BAM) was utilized to study lipid domain morphology to provide a molecular insight into how dipalmitoylphosphatidic acid (DPPA) molecules pack in the presence of divalent and trivalent cations. It was found that the trace metals exhibited strongest binding to the phosphate headgroup, followed by the carboxylate headgroup. By applying the Langmuir-Szyszkowski equation to binding fits, ion affinities for the phosphate headgroup were determined in the order of Al^{3+} > Fe^{3+} > Zn^{2+} > Mg^{2+} > Ni^{2+} > Mn^{2+} > Ca^{2+}. Thus, we conclude ion binding to phosphate groups plays a significant role in selective enrichment of trace metals at the SSML.
Research Project Title: Ethanol steam reforming on nickel-cerium oxide catalysts

Student Presenter: Joshua Graham

Faculty Mentor: Robert Baker

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Water and ethanol vapors react at high temperatures in an ethanol steam reforming reaction on nickel catalyst to evolve hydrogen as well as producing acetaldehyde, ethylene, methane and other carbon byproducts. This reaction is of interest because the production of hydrogen gas from a naturally produced source such as ethanol has direct renewable energy applications. The addition of semiconductors to steam reforming catalysts has been studied to examine the effects on product selectivity, catalytic rate enhancement and stabilization of the catalyst. In this study the effect of semiconducutive cerium oxide nanoparticles arranged in specific surface morphologies on a nickel surface was studied. The cerium nanoparticles were shown to change the selectivity and rate of the ethanol steam reforming reaction. The product distribution and rate of product turnover was studied using batch mode gas chromatography, while surface morphology was studied using X-ray photoelectron spectroscopy.
Research Project Title: Electrochemical performance of polymer and potassium salt electrolyte

Student Presenter: Justin Dilenschneider

Faculty Mentor: Yiying Wu

Faculty Mentor Department: Department of Chemistry and Biochemistry

Research Abstract: Current batteries require further research to fulfill the stability, cost, and energy requirements of modern technology. Potassium-oxygen batteries show promise in their large specific energy and high round-trip efficiency; however, further research is required to develop this technology. Using a salt-in-polymer electrolyte instead of an organic based electrolyte could improve the cycle life of the battery while retaining its efficiency and performance. As of yet, little research has been conducted to determine the performance of these salt-in-polymer electrolytes in potassium-oxygen batteries. We address this shortcoming by investigating important parameters including the cycle life, overpotential, columbic efficiency, and rate capability of a potassium-oxygen battery using these salt-in-polymer electrolytes.
Research Project Title: Synthesis and characterization of piezoelectric porous membrane support

Student Presenter: Shoko Kanemoto

Faculty Mentor: Hendrik Verweij

Faculty Mentor Department: Material Science Engineering

Research Abstract: Membranes are often used for water recovery in both industrial and municipal settings. One of the continuing issues during the operation is fouling which is induced by the accumulation of contaminants on the membrane surface or within the pores, degrading the water flux and filtration performance. The current defouling methods are not 100% effective, yet time consuming and costly as they may require equipment shutdown, membrane removal from the line, and use of chemicals. The piezoelectric porous membrane support can introduce a self-cleaning, fouling mitigation function to the membrane to avoid fouling, entirely. This material can generate ultrasonic waves when subjected to alternating voltage at the characteristic resonance frequency, and the subsequent cavitation and shear stress at the surface of the membrane inhibit the formation of the fouling layer. alpha-quartz is a piezoelectric material that is, lead-free, insoluble in water, and possesses permanent piezoelectric effect at its single crystal phase. The purpose of this works is to investigate the synthesis method of alpha-quartz (SiO$_2$) membrane support, and the characterization of its water filtration, mechanical resonance, and fouling mitigation properties. The silica was obtained as nanopowder and consolidated into a disk-shape by pressing, followed by thermal treating through sintering. The successful synthesis was achieved through the use of additives and granulation before pressing and sintering at the optimal pressure and temperature of 70MPa and 1400$^\circ$C, respectively. The crystalline phase was investigated under XRD, and the result was compared against calculated powder diffraction spectrum in Diamond. The vibrational frequency was studied through acoustic emission test and tank test, and analyzed with COMSOL modeling. The mitigation property was investigated through dead-end filtration testing. The development of this membrane support can offer more environmentally friendly solution to the problem of fouling and external cleaning process of the water filter membranes.
Research Project Title: The preparation of quinone methide precursors to re-alkylate aged acetylcholinesterase

Student Presenter: Ravali Kode

Faculty Mentor: Christopher Callam

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Organophosphorus (OP) compounds are known to have detrimental effects on the enzyme, acetylcholinesterase (AChE). AChE is found in the central and peripheral nervous system. This enzyme hydrolyzes the neurotransmitter acetylcholine (ACh) into choline and acetate. When AChE is exposed to OP compounds, such as pesticides or chemical nerve agents, it covalently inhibits and after a period of time goes through an aging process. When the enzyme is inhibited or aged, this leads to a buildup of acetylcholine in the body. In this state, the side effects include muscle twitches, reduced vision, paralysis, vomiting, convulsions, and eventually death. A group of compounds known as pyridinium oximes can reactivate the inhibited AChE. However, if there is prolonged exposure, the enzyme becomes de-alkylated and transitions from an inhibited state to an aged state. There are currently no known pharmaceutical treatments for this aged species. Our research focuses on developing a small molecule that can be used to re-alkylate the aged enzyme. Computational studies and literature show that compounds known as quinone methides (QMs) and quinone methide precursors (QMPs) have the ability to act as a re-alkylating agent. Our research involves synthesizing a family of QMP like compounds that can be used to re-alkylate aged AChE. Our current library of compounds consists of frameworks such as benzene, pyridine and pyrrole with varying functional groups. Varying these groups allows us to further analyze both electronic and steric interactions the compound has on the active site and how it affects AChE. The synthesis and screening of these compounds will be presented.
Research Project Title: Synthesis and characterization of Br double perovskite precursors: Cs2AgBr3 and CsAgBr2

Student Presenter: Nicholas Harvey

Faculty Mentor: Matt Gray

Faculty Mentor Department: Chemistry

Research Abstract: Renewable energy over the years has been of growing interest for many reasons. My research is focused on synthesizing lead-free halide materials and mapping out their phase diagrams. The specific phase diagram that has been of focus is the CsX, BiX, AgX (X= Br, Cl). This system has been of interest because of the interest in the double perovskite that can be made in the middle of these diagrams. The double perovskites are materials that are used in the applications of solar cells which aim to increase the efficiency of these cells. The bromine analogs of these materials have been made more pure than the chlorine versions.
Research Project Title: Polarity-reversal cascade for C-H functionalization of heteroarenes

Student Presenter: Xin Gu

Faculty Mentor: David Nagib

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Nitrogen-containing heteroarenes are medicinally important core in many therapeutic drugs. Applying and improving methods of C-H functionalization on existing drugs and drug candidates facilitates drug discovery and is a major focus on synthetic organic chemistry. Besides other methods for heteroarene C-H functionalization, Minisci reaction, in which a two-component coupling between a nucleophilic radical and an electron deficient heteroarene, is of interest and considered as a powerful tool for C-H functionalization. Typically, the generation of the nucleophilic radical is achieved via the oxidation of a weak C-H bond or halogen-abstraction. In the interest of examining new methods to generate nucleophilic radicals, that can be employed in the Minisci reaction, a three-component process has been developed and successfully employed to functionalize three classes of heteroarene substrates in moderate to good yields. This three-component Minisci reaction involves the generation of an electrophilic radical that upon addition to ethyl vinyl ether, generates the desired nucleophilic radical. This polarity-reversal cascade allows for additional functionality to be installed into the side-chains of compounds, whereas with the classical variant the radical precursors must be pre-functionalized, and allows for further derivatization of medicinally useful molecules.
Research Project Title: Synthesis, crystal structures, and magnetic properties of double perovskites containing 5d transition metals

Student Presenter: Nathalie Milbrandt

Faculty Mentor: Patrick Woodward

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Transition metal oxides containing 5d ions have exhibited many exotic magnetic properties, the underlying mechanism of which has not yet been fully understood. Many of the unique characteristics of 5d transition metal oxides are thought to be dependent on the strong spin orbit coupling and the extended d orbital. Double perovskites provide a great platform to study the magnetic interactions among 5d transition metal ions because they are amenable to various types of element substitutions. For 5d1 and 5d2 electron configurations, diversely exotic magnetic properties have been found such as ferromagnetism, antiferromagnetism, and spin glass. Octahedrally coordinated transition metal ions with a 5d4 configuration should possess a nonmagnetic J=0 state due to the effects of strong spin orbit coupling, however, recent studies by different groups have shown that there exists nontrivial magnetic moments in some compounds. By synthesizing new double perovskites containing 5d transition metals, the exotic magnetic properties can be explored.

Solid state synthesis has been performed on targeting stoichiometry of and Ba2MIrO6 (M= Lu, and Fe) and SrLaMIrO6 (M= Zn, Mg, and Ni) which are all in a d4 electron configuration. The crystal structures of the products have been studied using X-ray powder diffraction. The Ba2FeIrO6 crystallizes in a hexagonal structure, the Ba2LuIrO6 crystallizes in a cubic double perovskite structure, and all the other iridates crystallize in a monoclinic double perovskite structure. Preliminary magnetic data shows that Ba2LuIrO6, SrLaZnIrO6, and SrLaMgIrO6 are paramagnetic and SrLaNiIrO6 is likely antiferromagnetic. Further magnetic data and heat capacity data are needed for these as well as the other iridates to determine and verify their magnetic properties. This study is expected to expand our knowledge of the interesting magnetic phenomena presented by 5d transition metal oxides in different crystal structures and with different B site cations.
Research Project Title: From feedstocks to medicines: new protocols for use of acrylates and dienes for the synthesis of valuable chemical intermediates

Student Presenter: Milauni Mehta

Faculty Mentor: Thaliyil Rajanbabu

Faculty Mentor Department: Chemistry

Research Abstract: Cobalt catalyzed heterodimerization of readily available conjugated dienes and alkyl acrylates affords a highly enantioselective heterodimerized product which can then be used in pharmaceutical and fine chemical synthesis. Known optimal conditions for this reaction include treatment of conjugated diene (1.00 eq) and methyl acrylate (1.10 eq) with isolated catalyst 1,3-bis(diphenylphosphino)propane cobalt dibromide \([\text{DPPPCoBr}_2]\) (0.05 eq), activator NaBARF (0.075 eq) and reducing agent Zn\(\text{A}^+\) (0.50 eq) in 0.15 M in dichloromethane [DCM] at room temperature for 4 hours, affording an isomeric mixture of the heterodimerized product in a 4:84:12 ratio as determined by GC analysis. Limitations for this reaction include the expensive cost of synthesizing NaBARF, excess use of Zn\(\text{A}^+\) and long reaction times. We have discovered a cost-efficient substitute, InBr3, for the activator NaBARF as well as a more environmentally friendly substitute, Li3N, for the Zn\(\text{A}^+\) reducing agent. This project involved scanning activators and reducing agents as well as their equivalence with respect to catalyst to create new optimal conditions for the heterodimerization reaction. The optimal condition was determined to be treatment of 1,3-(E)-undecadiene and methyl acrylate with the racemic ligand DPPP or chiral ligand (S,S)-BDPP (0.05 eq.), cobalt salt (0.05 eq.), reducing agent Li3N (0.10 eq.) and activator InBr3 (0.10 eq) in DCM (0.35 M) at room temperature to afford an isomeric mixture of the same ratio distribution as known conditions. The major isomer, the 1,4-addition product, was characterized via GC, GC-MS, 1H-NMR, and 13C-NMR. The reagents for these optimized conditions are readily purchasable thus significantly reducing the costs of the reaction. These conditions were expanded to functionalized substrates with varying degrees of conversion. The heterodimerized product has an \(\text{Î±,ß}-\)unsaturated carbonyl which can then be further functionalized via Michael addition or cyclization reactions which provides synthetic utility for medicines and valuable chemical intermediates.
Research Project Title: Development of advanced multifunctional polymer binders for cathode materials in lithium-ion batteries

Student Presenter: Adam Schmidt

Faculty Mentor: Jung-Hyun Kim

Faculty Mentor Department: Mechanical and Aerospace Engineering

Research Abstract: Reducing costs and improving environmental friendliness for the manufacturing processes of lithium-ion (Li-ion) battery cells are important goals of today’s battery research. Presently, the industry standard polyvinylidene fluoride (PVdF) binder “the glue holding the electrode together” requires a toxic solvent, N-methylpyrrolidone (NMP), during the electrode fabrication processes. Since the purchase and proper disposal of NMP contributes about 13% of the total cost for Li-ion battery production, finding a water-soluble replacement for PVdF would be economically beneficial. The purpose of this research is to develop an effective binder material that uses a water-based solvent, so that currently used toxic solvents can be phased out, reducing cost and increasing environmental friendliness. Lithiated polyacrylic acid (LiPAA), a possible alternative binder, uses a water-based solvent and has other desirable properties, such as increased adhesion force, increased cycle life, and decreased capacity fade. LiPAA is not currently a feasible binder, however, because electrodes produced using LiPAA are particularly brittle, which causes cracking during the battery manufacturing process, leading to reduced cycle life. In order to alleviate this undesirable mechanical behavior, LiPAA will be doped with styrene-butadiene rubber (SBR) and sodium alginate (Na-Alg). We hypothesize that adding these elastic materials to the brittle LiPAA will provide the electrode with the desirable electrochemical properties of LiPAA, while mitigating its brittleness. We will apply various compositions of LiPAA, Na-Alg, and SBR binders to a LiNi0.5Mn1.5O4 cathode. We will assess the quality of the coating and microstructure using scanning electron microscopy (SEM). We will fabricate cathodes with different binders into coin-type Li-ion battery cells to measure electrochemical performance. We will examine the effects of binder composition on the physical and electrochemical properties of cathodes in Li-ion batteries. We expect to find a water-soluble binder that facilitates the transfer of electrons without causing the electrode to fail through brittle fracture.
Research Project Title: Electrocatalytic properties of hydrogen absorbing Zintl phases

Student Presenter: Dominic Ross

Faculty Mentor: Josh Goldberger

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Low abundance of platinum and palladium, alongside the increased need for environmentally conscious energy options, such as fuel cells, has brought low cost catalysis to the forefront. However, to date there has been a lack of much investigation into novel catalysts beyond platinum alloys. Our work seeks to demonstrate the viability of novel Zintl phase catalysts and their hydrides (e.g. BaGa2 & BaGa2H2, BaGaGe & BaGaGeH) for electrocatalytic half reactions of interest to upcoming energy technologies, such as proton exchange membrane fuel cells which currently require high platinum loading. BaGa2H2 is expected to demonstrate excellent catalytic properties, and serves as a model system for the general reactivity trends of Zintl phase compounds before and after hydrogenation. Here, we measure the catalytic activity for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) of BaGa2 and its hydride by cyclic voltammetry, as well as investigation of the catalytic activity of GdGa for HER. In addition, we are investigated methods for electrochemical growth, from solution phase metal salts, of Zintl phases with small domain size and high surface area available for catalysis. Furthermore, by use of a sacrificial hydrogen source and applied electric potential, we attempt development of a method to electrochemically hydrogenate Zintl phase compounds.
Research Project Title: Synthesis of quinone methide precursors as acetylcholinesterase reactivators

Student Presenter: Sydney Sillart

Faculty Mentor: Christopher Callam

Faculty Mentor Department: Chemistry

Research Abstract: Organophosphorus (OP) agents are responsible for the inhibition of the enzyme acetylcholinesterase (AChE). AChE is responsible for the hydrolysis of the neurotransmitter acetylcholine. OPs are covalent inhibitors of AChE and have been used as chemical warfare agents as well as pesticides. Without functioning AChE, acetylcholine accumulates and leads to serious adverse health effects, such as vomiting, paralysis, and even eventual death by respiratory failure. The magnitude of the effects and rate of death are determined by the OP’s toxicity. There are known therapeutics, called pyridinium oximes, which can reverse the inhibition and reanimate AChE if administration occurs before aging. If left untreated, aging will occur, which is a dealkylation of the OP that is bound in the active site. Aging causes the OP to form a highly stable, charged alkyl phosphonate. There are currently no effective treatments to reverse the aging process, as aged AChE is unresponsive to reactivation by pyridinium oximes.

Our research focuses on synthesizing and testing small organic compounds that can hopefully re-alkylate the aged enzyme and enable it to be activated by pyridinium oximes. Quinone methide precursors (QMPs) are of particular interest because their structure resembles that of other molecules that are capable of binding to the active site of AChE. Furthermore, QMPs have been shown to have the ability to alkylate DNA, so they could potentially realkylate aged AChE as well. Their reactivity can be intensified by addition of other functional groups to their framework. Many libraries of QMPs have been synthesized, specifically libraries derived from different quinolone and isoquinoline frameworks. The aim is that one of these derivatives synthesized will be the key to realkylating aged AChE efficiently, and eventually lead to the reactivation of the enzyme. We will present multiple synthetic efforts towards the assembly of QMPs and screening assays with aged AChE.
Research Project Title: Synthesis and evaluation of pyridine based quinone methide precursors for aged acetylcholine esterase reactivation

Student Presenter: Jenna Tabbaa

Faculty Mentor: Christopher Callam

Faculty Mentor Department: Department of chemistry and biochemistry

Research Abstract: Organophosphorus compounds (OPs) such as tabun, sarin and soman are used as chemical warfare nerve agents. The advancements of chemical warfare agents used for military tactics exceed the research to inhibit the effects of the nerve gases. The demand to study OP nerve agents is crucial because of the damaging effects to people, the commercial availability, and even the stockpiles in countries. Exposure to OPs affects the central nervous system and causes a buildup of acetylcholine in the body by inhibiting acetylcholinesterase (AChE). The AChE is initially inhibited followed by an aging process. There are known therapeutic oximes for inhibited AChE, pyridinium oximes; however, there are no known treatments for aged AChE. We are developing a library quinone methide precursors (QMPs) to be used as potential re-alkylators. These QMPs can be used to potentially re-alkylate the aged OP-AChE complex followed by reactivation. This research is vital to enhance the pharmaceutical measures and further inspire more research done to medically counteract the aging process. Several frameworks were synthesized through synthetic routes including nucleophilic substitution, reductive amination, and Mannich reactions. We will present the synthesis of a small library of pyridine QMP frameworks and the screening of these compounds as re-alkylators and re-activators of both the inhibited and aged AChE (electric eel and human).
Research Project Title: Five-member ring heterocycles as aged acetylcholinesterase therapeutics

Student Presenter: Nathan Yoshino

Faculty Mentor: Ryan Yoder

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Organophosphorus compounds (OPs) are widely implemented as chemical nerve agents and pesticides. These OPs bond to and inhibit a catalytic residue, Serine-203, in the enzyme acetylcholinesterase (AChE) which is responsible for the hydrolysis of acetylcholine. After exposure to OPs, AChE is initially inhibited for a period of time followed by an aging process, wherein the inhibited Ser-203 residue dealkylates and forms a stable phosphonate anion in the active site. There are known treatments for inhibited AChE in the form of therapeutic oximes, but no treatments for aged AChE currently exist. If left untreated, acetylcholine will build up in the central nervous system. Previous research has demonstrated quinone methides to realkylate phosphonates and other biological molecules, and currently a lead compound in the form of a quinone methide precursor (QMP) has been found. This research studies the potential of QMPs and QMP like compounds to realkylate the stable phosphonate anion on Ser-203 in aged AChE and allow for subsequent reactivation.

Using computational methods, libraries of QMPs and QMP like compounds were tested to determine their affinity for the aged AChE active site. The computational methods Molecular Docking and Molecular Dynamics were used. In Molecular Docking, poses of lowest energy conformations of a ligand within the aged AChE active site were generated and analyzed. The generated poses reveal how the ligands interact with the enzyme and provide structural insight to the success of certain QMPs. In addition, the distance from the aged serine residue to the ligand will be measured. Molecular Dynamics evaluates the ligands’ interaction with the enzyme over time in a fluid environment. Using the most favorable poses from Molecular Docking, the ligands were simulated to interact with the ligand over 1 nanosecond. The results from Molecular Dynamics will be used to determine which section of the enzyme that the ligand spends most of its time. Ligands that favor the active site are the most promising realkylators.

In addition to computational studies, ligands that have shown high affinity with the active site were synthesized. The ligands were synthesized through synthetic routes including nucleophilic substitution, amidation, and Mannich reactions and were characterized by nuclear magnetic resonance spectroscopy (1H and 13C) and high-resolution mass spectrometry. These compounds were exposed to aged AChE with a therapeutic oxime to determine the reactivation.

With no known treatments for aged-acetylcholinesterase, this research intends to find compounds that can effectively and practically realkylate aged AChE to treat the thousands affected by OPs each year. Computational methods will be used to identify QMPs with high potential for realkylation. Target compounds will be synthesized in the laboratory. Once synthesized, the compounds will be tested to determine their realkylation in vitro.
Research Project Title: Study of fluorinated quinone methide in the resurrection of aged acetylcholinesterase

Student Presenter: Dennis Yang

Faculty Mentor: Christopher Callam

Faculty Mentor Department: Chemistry

Research Abstract: The recent usages of the organophosphorus (OP) nerve agent sarin in chemical warfare, as well as the longstanding concerns regarding the toxicity of OP-based pesticides, has brought OP compounds into the limelight. The toxicity of OPs is founded in their ability to inhibit acetylcholinesterase (AChE), the enzyme involved in the hydrolysis of a key neurotransmitter, acetylcholine. Inhibited AChE is subsequently dealkylated in a process referred to as aging. Standard decades-old treatments involving atropine and oximes are only capable of treating inhibited AChE to a limited extent; moreover, no known drugs are capable of reviving or treating aged AChE. These facts present the urgent need to develop a therapeutic agent or combination thereof that is capable of re-alkylating aged AChE and more effectively reactivating inhibited AChE. In recent years, our research team has established a quinone methide precursor with a pyridine framework that has demonstrated unprecedented efficacy in resurrecting aged AChE—"that is, converting aged AChE to its native state. Our work has further indicated a pH effect on performance. In this present study, a variety of our leading compounds were fluorinated in the prospects of optimizing performance; fluorine was chosen for its well-documented capabilities of favorably affecting pKa, intrinsic potency, and permeability of pharmaceutical agents. The compounds were synthesized, characterized via NMR and MS to ensure identity and purity, then screened with human and electric eel AChE to evaluate therapeutic effectiveness. The results of the screening will be discussed in depth at the convention. Presently, research efforts have shifted to the synthesis of a new target molecule, 2-(aminomethyl)pyridin-3-ol, that will allow access to a host of novel reaction pathways, in the aspiration of identifying compounds that have an even greater efficacy in treating OP exposure.
Research Project Title: Effect of sulfur-containing dopants on filling efficiency for conducting polymers

Student Presenter: Victoria Yee

Faculty Mentor: Vishnu Sundaresan

Faculty Mentor Department: Mechanical Engineering

Research Abstract: Cellular physiology is sensitive to minute changes in the chemical composition of its environment. Therefore, understanding the effect of ionic concentration is significant to understanding healthcare (diagnosis and treatment). Electrically conductive polymers, such as polypyrrole, exchange ions with solution by the application of electrical potentials and thus alter the chemical composition of the solution without the use of microfluidics. Calculation of morphology-dependent parameters, such as filling efficiency, assists in quantifying these transport phenomena. In an effort to understand how conducting polymers may influence cellular physiology, a conducting polymer’s cation storage capacity was measured to calculate the ability of the conducting polymer to change the chemical makeup of an ionic solution. Polypyrrole samples were fabricated using three dopants (p-toluene sulfonate, dodecyl sulfate, and dodecylbenzenesulfonate) at charge densities of 0.4 C/cm^2, 0.8 C/cm^2, and 1.2 C/cm^2. These membranes were pretreated with cyclic voltammetry until all ion exchange was reversible and then characterized by chronoamperometry. All tests were conducted with 100mM potassium chloride solution. The number of ions exchanged by polypyrrole with the solution was calculated by fitting the data to an exponential function used to describe ion transport and compared to the theoretical maximum ion storage of the polypyrrole film. Preliminary findings indicated that filling efficiency (ionic ingress divided by the theoretic maximum) was approximately equal across all dopants. As all three dopants possess a similar morphology, they form polymers with a comparable number of redox sites, and filling efficiency is largely dependent on the number of available redox sites. These findings establish that the filling efficiency of polypyrrole is independent of the dopant for a given dopant morphology.
Research Project Title: Azo dyes as ionochromic anion indicators

Student Presenter: Sydney McKee

Faculty Mentor: Noel Paul

Faculty Mentor Department: Chemistry and Biochemistry

Research Abstract: Organic azo dyes, which contain the nitrogen-nitrogen double-bonded azo functional group (-N=N-), have found wide use as valuable textile dyes, tissue stains, and pH indicators. These highly conjugated systems can be synthesized via the electrophilic substitution of activated aromatic rings with arenediazonium salts, resulting in molecules that exhibit high molar absorptivities within the visible light range. Originally, it was thought that structures based on 1,8-bis(dimethylamino)naphthalene may have led to dyes that could exhibit ionochromic sensitivity to various aqueous anions. However, it was found that potential dyes containing this motif were impure and difficult to isolate. This structure was thus abandoned in favor of coupling the diazonium salts with a wide variety of nucleophiles in both aqueous and organic media in order to find an optimal synthetic strategy. Particularly pure dyes were exposed to varying pH and anion concentrations in a range of solvents, and the changes of their UV-vis spectra were assessed. These experiments have provided guidance for the identification of future candidates for further analysis. In the context of water sanitation and health, a successful indicator would serve as a facile and cost-effective method of identifying hazardous anion concentrations in drinking water.
Research Project Title: Radical-mediated, one-pot synthesis of oxazoles from alcohols and nitriles

Student Presenter: Darsheed Mustafa

Faculty Mentor: David Nagib

Faculty Mentor Department: Chemistry

Research Abstract: Heterocycles are found in many classes of natural products, pharmaceuticals and materials. In pharmaceutical development, investigating a diverse library of compounds can provide a rapid and effective way to screen for lead compounds and identify beneficial pharmacophores via structure-activity relationship analyses. Thus, the rapid assembly of heterocycles with divergent functionality is an important focus in organic and medicinal chemistry. Oxazoles are one class of aromatic heterocycles that have shown interesting anticancer and anti-fungal properties. In general, oxazoles have been synthesized using a variety of methods. Some noteworthy limitations of these preparations include using starting materials that are not readily available, and incorporating harsh conditions such as the use of very strong acids (HCl & H2SO4) or elevated temperatures. Noting these drawbacks, we hypothesized that we could take advantage of chemistry previously developed in our laboratory for the b-selective C-H amination of alcohols. Our new method involves addition of an alcohol into nitriles to form an imidate. This imidate then undergoes b-selective amination to provide an intermediate oxazoline heterocycle, itself a valuable structural motif in some classes of pharmaceuticals. The intermediate oxazoline is then further oxidized in situ to access differentially substituted oxazoles. This strategy provides rapid access to a library of heterocycles with privileged architectures found in anti-cancer medicines.
Research Project Title: Improved stability of a C-C bond coupling catalyst for thermal CO2 fixation

Student Presenter: Skyler Ware

Faculty Mentor: Robert Baker

Faculty Mentor Department: Chemistry

Research Abstract: The electrochemical conversion of carbon dioxide to value-added, multi-carbon products has been studied as a pathway to renewable fuel sources and as an alternative to current carbon capture and storage methods. Delafossite copper iron oxide films have been shown to thermally fixate carbon dioxide and selectively catalyze C-C bond coupling from CO2 to produce acetate. However, the catalyst alone is not stable and deactivates after approximately ten minutes following the reductive dissolution of surface iron species. The addition of gaseous oxygen as a sacrificial electron acceptor prevents the reductive dissolution of iron and stabilizes the catalyst for several hours; however, excess oxygen scavenges the electrons used for acetate production, resulting in lower yield and reduced conversion efficiency. The purpose of this study was to determine the optimum oxygen flow rate to maximize acetate production while minimizing catalyst deactivation. An electrolyte solution was purged with both carbon dioxide and oxygen before and during electrolysis using the copper iron oxide catalyst as the working electrode. The carbon dioxide flow rate was held constant, while the oxygen flow rate was varied over several trials. Acetate production was quantified by 1H-NMR spectroscopy, and the post-reaction catalyst was characterized by XPS and SEM/EDX imaging. The optimal oxygen flow rate significantly slowed iron reduction and stabilized the catalyst for up to 12 hours with only a modest drop in acetate selectivity. This enhanced stability will allow further examination of the surface chemistry over long-term reductions, including the mechanism of acetate production and the role of both metals in the catalytic process.
Research Project Title: From feedstocks to value-added chemicals: a mechanistic study of a cobalt-catalyzed reaction between 1,3-dienes and acrylates

Student Presenter: Montgomery Gray

Faculty Mentor: Rajanbabu Yes

Faculty Mentor Department: Thaliyil

Research Abstract: Powerful methods have been developed to provide a diverse set of intermediates for the synthesis of pharmaceuticals and other fine chemicals. In particular, 1,3-dienes can be functionalized into enantiopure 1,4-dienes through cobalt catalyzed-heterodimerization with either ethylene or methyl acrylate. Since these precursors are abundantly available and, the chemistry highly selective, such reactions provide inexpensive routes to value-added intermediates. The optimization of the reaction conditions for large-scale synthesis depends on a deeper understanding of the mechanism of the reaction, which is still not entirely understood. Traditional kinetic analysis can provide insights on mechanistic details, but often does not suffice to provide a complete picture of this system because of accompanying side reactions in the process, deactivation/inhibition of the catalyst, and the lack of continuous data as the reaction progresses. Therefore, a kinetic study using reaction progress kinetic analysis (RPKA) was performed on the cobalt catalyzed hydrovinylation reaction to aid in the determination of the mechanism of the reaction. In-situ infrared spectroscopy is used to collect data for the system allowing for continuous concentration data to be obtained. The reactants, catalytic system, and solvent chosen for this study were 2,3-dimethyl-1,3-butadiene and methyl acrylate, 1,3-bis(diphenylphosphino)propane cobalt (II) bromide, zinc powder, and zinc bromide, and dichloroethane respectively. The possibility of catalyst deactivation with time, catalyst deactivation due to product and ligand interactions, and deactivation due to the reagents used are specifically examined during this study. The experimental data suggest that the reaction is inhibited by neither the ligand, product, nor the acrylate, but instead, the reaction is inhibited by the diene. Future studies will examine how this reaction can be improved using the new found understanding of its kinetics and mechanism.