Synthesis of Novel Inhibitors For Low Molecular Weight Protein-Tyrosine Phosphatase
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*Biochemistry, Chemistry*

Protein tyrosine phosphatases (PTPs) are a group of enzymes that remove phosphate groups from phosphorylated tyrosine residues on proteins. A specific PTP, Low molecular weight protein tyrosine phosphatase (LMW-PTP), impacts processes such as embryonic development and tumor dispersion. Its over expression in the cell also leads to increased cellular motility as well as invasiveness. The effects of LMW-PTP on various biological processes make it a target for a diverse set of small molecule inhibitors. A known natural product inhibitor of LMW-PTP is pyridoxal-5’-phosphate (PLP). PLP displays tight binding to LMW-PTP with a docking score of -7.266 and a $K_i = 7.6 \, \mu M$ (pH 5.0), but lacks the specificity required to be an effective inhibitor. The scope of this research is to model inhibitors of LMW-PTP human isoform II after the natural product PLP, specifically carboxylic acid derivatives of the structure. These analogues will be tested in vitro using a biological assay.

The Effect of Seasonal Changes in Water Composition and Inorganic Salt Buffers on the Degradation of Trichloroethylene
Graci M Gorman
*Chemistry*

The purpose of the research was to explore how seasonal changes in water composition affect the degradation rates of the known water contaminant and carcinogen, trichloroethylene (TCE). This was done by monitoring the degradation of TCE in natural water and by running the degradation reactions with added inorganic salts or in buffered water and comparing those results to the rate of TCE degradation in just DI water. TCE was reduced to ethane via a rhodium on alumina catalyst under a hydrogen atmosphere. Gas Chromatography headspace analysis was used to analyze the kinetics of the reaction, more specifically, the rate of TCE degradation. The degradation rates proved to be relatively similar between the seasons, while the inorganic salts and buffers had a greater impact on reaction kinetics. The phosphate buffer had the most significant accelerating effect relative to the deionized water reaction, while the nitrite, sulfite, and phosphite buffer halted the reaction. These results indicate the importance of considering water composition when implementing this degradation method in a large-scale environment.

Separation of free Amino Acids using reverse phase HPLC
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Analysis of free amino acids is a promising approach for targeted metabolomics and many pathological conditions. HPLC offers the separation and quantification of multiple amino acids simultaneously. An isocratic method was developed for separation of aspartic acid, alanine, glutamic acid, tyrosine, glycine, leucine, isoleucine, and phenylalanine using reverse phase HPLC. The amino acids were derivatized with
ortho-phthalaldehyde and detected at 190 and 338 nm. A separate gradient method was also developed for separation and detection of oxidized boc-tryptophan from its non-oxidized form.

**Synthesis of phosphonate analogs of pyridoxamine as potential inhibitors of LMW-PTP**

Harry J Gerdes  
*Biochemistry, Chemistry*

Low molecular weight protein tyrosine phosphatases (LMW-PTPs) are enzymes that have been linked to cellular transformation. In addition, the overexpression of LMW-PTP in tumor cells has been recently shown to induce neoplasticity in nontransformed cells. Furthermore, LMW-PTP human isoform B has been demonstrated to be oncogenic. The docking of pyridoxal 5'-phosphate (PLP), a strong competitive inhibitor of LMW-PTP, with LMW-PTP isoform B was examined. Phosphonate analogs of pyridoxamine, where the aminomethyl group is modified with different aromatic groups and the 5'-position converted to a phosphonic acid group, were screened virtually. These analogs were then synthesized and tested via an in vitro kinetic assay with LMW-PTP isoform B. The data from this study will be presented.

**Observing Protein-Nanoparticle Interactions using Dynamic Light Scattering (DLS) technique**

Charles C Dudek  
*Chemistry*

Nanotechnology has grown tremendously over the last two decades in the fields of medicine, cosmetics, and electronics. Despite huge development in the production of nanoparticles, little is known about their interactions with biomolecules within organisms. Protein-nanoparticle interactions is a new area of study that focuses on the structural and functional changes of proteins when they are introduced to nanoparticles. Spectroscopic and calorimetric methods have been used comprehensively to describe these interactions. Specifically, this paper discusses the applications of Dynamic Light Scattering (DLS) compared to other techniques available in monitoring protein-nanoparticle interactions.

**Analysis of the Photodegradation of Pharmaceuticals in Aqueous Solutions using HPLC**

Sara B Matthews  
*Chemistry*

The photodegradation of pharmaceuticals is of environmental concern, as the disposal of these drugs is not well-regulated, and compounds for human consumption can accumulate in the environment, especially in lakes from wastewater runoff. Six pharmaceuticals; acetaminophen, phenylephrine HCl, chlorpheniramine maleate, aspirin, amitriptyline HCl, and nortriptyline HCl, were analyzed to see if these compounds will degrade when exposed to sunlight. This was done in aqueous solutions of differing pH (3, 5, and 9) using a photoreactor. The degradation and product formation was monitored using an HPLC to observe if any stable decomposition product formed, and to determine the half-life of these compounds in sunlight. The effect of pH on the degradation of these pharmaceuticals and their resulting
half-lives was also explored. Of the six compounds, amitriptyline HCl had the fastest degradation while phenylephrine HCl had the slowest.

**The effect of pH on the hydrodechlorination rate of trichloroethylene by Rh/Al2O3 catalysis**
Kaitlyn E Lauer  
*Chemistry*

Trichloroethylene (TCE) is an anthropogenic chlorinated hydrocarbon compound that has become an increasingly abundant groundwater contaminant. The heavy metal catalyzed hydrodechlorination of TCE to ethane is an established method of detoxification. This study compares the effect of acidic, basic and neutral phosphate buffers on the Rh/Al2O3 catalyzed hydrodechlorination of TCE in deionized water under a hydrogen atmosphere. The degradation rate of TCE was determined using gas chromatography headspace analysis. The purpose of this study was to determine how the pH affects the rate of the hydrodechlorination reaction. The reaction was run at pH 2, pH 7 and pH 11; all other parameters were held constant. The influence of pH on the hydrodechlorination reaction rate may have important implications for large-scale groundwater treatment mechanisms.

**A paper based device for colorimetric quantification of free amino acids in biofluids**
David R Crotteau  
*Chemistry*

Paper-based bioassays provide a convenient, low-cost alternative for many applications such as clinical diagnosis, food quality control, and environmental monitoring. In this study, we have developed and optimized a paper-based colorimetric assay for the detection of free amino acids in biological samples. The new method takes advantage of the redox properties of cerium (IV) oxide nanoparticles along with the enzymatic specificity of l-amino acid oxidase, and was applied to the determination of free amino acid concentrations in simulated saliva samples.

**Synthesis and in vitro assays of benzimidazole analogues as potential inhibitors of LMW-PTP**
Blake P Belland  
*Biochemistry, Chemistry*

Human low molecular weight protein tyrosine phosphatases function in the control of cell growth. Over expression of LMW-PTPs has shown to cause tumor growth. Using virtual and in vitro screening processes, 9H-purine-2,8-diamine (Kis 31.7±8.2 μM) was shown to be an effective inhibitor of LMW-PTP isoform B. Benzimidazole analogues of 9H-purine-2,8-diamine, 1H Benzimidazole-2,6-diamine and 6-aminobenzimidazole, were synthesized and tested using an in vitro assay. These analogs were chosen in order to observe the change in inhibition as the hydrogen bonding changed from the original compound. Molecular modeling of their structures was performed to determine their docking scores. Kinetic assays were used to determine the inhibition constants of these compounds and therefore determine their effectiveness as an inhibitor of LMW-PTP isoform B.
Synthesis and Study of Silver Nanoparticles
Brett L Anderson
Chemistry

The goal of this experiment was to determine the best method to synthesize silver nanoparticles for use as a potential experiment in the synthesis lab. The nanoprisms synthesized vary from 10-70 nm in width depending on the concentration of potassium bromide and will remain stable at these small sizes. These nanomaterials have optical properties different from larger particles. The nanomaterials need to be made precisely to stabilize the nanoparticles size. The nanoparticles form three distinct colors at different sizes. From 10-30nm the nanoprisms are yellow/orange, from 30-50nm the nanoprisms are purple, and from 50-70 the particles are blue. The varying sized particles are put through a UV-Vis spectrometer to determine at what wavelength of light they absorb. It can be understood by this process how size of the particles can affect the wavelength a particle absorbs and understand why the particles appear different colors with varying size.

Polymerization: Lab Development
Erin O Wissler
Chemistry

Not only are polymers the backbone of a plethora of everyday products, but they also have a multitude of fascinating chemical properties that make them wonderful tools for learning important fundamentals of organic chemistry. This project analyzed the ring opening chemistry of D, L-lactide, γ-butyrolactone, valerolactone, dodecalactone and caprolactone. Starting with each of the above monomers, Sn(Oct)2,SnCl2, Zn(acac)2, ZnCL2, and AlCl3 were used as catalysts in the polymerization process. Initiators included benzyl alcohol, 2-phenylethanol and 1-butanol. The results of each reaction were analyzed by 1H-NMR and IR spectroscopy and dynamic light scattering (DLS). The results were collated to determine the most promising candidates for a student project in the teaching laboratory.

Effect of Sulfuric Acid Coating on Common Mineral Dusts
Miguel D Mendoza
Chemistry, Experiential Learning & Community Engagement, Undergraduate Research

Mineral dust has a large effect on cloud formation and ultimately the climate. Several studies have shown the addition of acid to these mineral dust particles decreases their ability to nucleate ice. This study explores what chemistry occurs between common components of mineral dust particles and sulfuric acid. Hematite (Fe2O3), calcite (CaCO3), and quartz (SiO2) were exposed to sulfuric acid, and then analyzed using a combination of Attenuated Total Reflectance-FTIR, Diffuse Reflectance-FTIR Spectroscopy, X-Ray Diffraction, and Inductively Coupled Plasma Atomic Emission Spectroscopy to identify functional groups, mineral species, and aqueous phase elements. Quartz did not react with sulfuric acid. Calcite and hematite react readily with sulfuric acid to produce bassanite (CaSO4•1/2H2O) and rhomboclase (H3O+) Fe(SO4)2•(H2O)3 respectively. Knowing how sulfuric acid affects these common mineral dust particles helps us understand how they age in the atmosphere and the effect on
climate from this aging. Future experiments will explore other mineral dust components and eventually relate what chemical changes affected ice nucleation abilities.

MacMillan-Type Reactions Using Dendrimer-Bound Catalyst
Carla M Saunders
Chemistry, Undergraduate Research

Dendrimers present an attractive option for use as catalytic framework. In particular, terminally functionalized dendrimers present the possibility of increased catalytic utility and recovery. Generations two, three, and four PAMAM dendrimers have been functionalized with MacMillan’s (2S, 5S)-5-benzyl-2-tert-butyl-3-methyl-imidazolidin-4-one catalyst sites. These functionalized PAMAM dendrimers were characterized by NMR and MALDI-TOF analysis. We are now investigating these dendrimers for their effectiveness as catalysts in MacMillan-type organo-catalytic reactions including an Aniline addition reaction and a Diels Alder reaction done by the MacMillan group.

Characterization of Poly(lactide-b-butadiene-b-lactide) Multiblock Copolymers
Sean T Pickthorn
Chemistry

Recent advances in polymer production sciences have led to an increase in research in sustainable practices. Our efforts intended to produce a toughened biorenewable multiblock copolymer. Polylactide has been noted to be produced by sustainable practices but is limited because of the fragile structure. To improve the brittle behavior of polylactide, preparation of polylactide-b-polybutadiene-b-polylactide multiblock copolymers were synthesized with a fixed weight of dihydroxyl polybutadiene (~3000 and ~2000g/mole series) and variable volume percent (50-90%) of both semicrystalline poly(L-lactide) and amorphous poly(D,L-lactide). Producing a multiblock copolymer was intended to strengthen the mechanical properties by bridging and gapping over several domains. Initially, triblock polymers were catalyzed with a ring opening polymerization and characterized. Toluene diisocyanate (TDI) and terephthaloyl chloride (TCL) were used to couple the triblock copolymers to form multiblock structures. Characterization of these products was accomplished by differential scanning calorimetry, small angle X-ray scattering, 1H-NMR spectroscopy, size exclusion chromatography, dynamic mechanical analysis, and tensile testing, leading to an extensive set of thermal and mechanical properties of both the triblock and multiblock copolymers. The data collected indicated a controlled product with a clear enhancement of mechanical properties of polylactide. Trends associated with the weight percent of polylactide can be used to guide future work as we explore other aspects of this material. [This research was supported by funding from the NSF, awarded to the Center for Sustainable Polymers, University of Minnesota, Minneapolis, MN]
Optimization of Variables in Trinitroresorcinol Production
Ellen M Dean
Chemistry, Experiential Learning & Community Engagement, Undergraduate Research

Federal Premium Ammunition produces cartridges that contain a bullet, case and primer. The bullet is a solid metal tip that is propelled by the fuel in the case and the explosives found in the primer. The primer is a small capsule in the back of the cartridge that is filled with explosives to propel the cartridge out a gun barrel and ignite the gunpowder in the case. This research focused on improving the production process of trinitroresorcinol (TNR), one of the explosives used in primers, by optimizing variables from the current standard operating procedures. The production of TNR is a two-step process including sulfonation and nitration of the starting material, resorcinol. Manipulated variables include run time, acid ratios, different starting materials and temperature ranges. All samples were analyzed by an explosive test, melting point and crystal size analysis. Results showed higher concentrations of nitric acid and higher temperatures ranges created TNR with bigger, more pure crystals.

Metal complexes--Efficient Catalysts for Light-driven water oxidation
Yuan Huang
Chemistry

Hydrogen will be one of the most important fuels of the future. The ideal way to obtain hydrogen is by splitting water rather than obtaining it from petroleum. Water oxidation forms oxygen, protons, and electrons (equation 1), \(2H_2O \rightarrow O_2 (g) + 4H^+ + 4e^- \) and hydrogen is produced when the water oxidation process is coupled with proton reduction. Therefore water oxidation is seen as one of the most promising methods of storing energy from the sun, producing hydrogen as a green fuel. Traditionally, water oxidation has been accomplished thermodynamically. In order to avoid using fossil fuels, researchers have investigated light-driven water oxidation with energy from the sun providing the energy for oxidation. Since overpotential is the main concern during the water oxidation process, an efficient catalyst is needed. The catalyst is used to activate an oxidant, which oxidizes the water. There are two types of catalysts that can be used in water oxidation: homogeneous metal complexes and heterogeneous metal complexes. Precious metals such as ruthenium and iridium were first used as catalysts since those metals are often more active and can be sustainable when recycled. Because of economic concerns, common metals such as manganese, iron, and copper have also been used as catalysts. In this presentation, light-driven water oxidation mechanisms will be discussed for both homogeneous and heterogeneous metal complexes. Additionally, the potential future for light-driven water oxidation will be discussed.