Chemistry Department

Professor Jeffrey P. Fitzgerald
Chairman

The 2004-2005 Academic year saw the Naval Academy's Chemistry Department move into over 50,000 square feet of fully renovated office, classroom and laboratory space in Michelson Hall. Because of an aggressive building schedule and delays caused by Hurricane Isabel flooding (September 2003), the new laboratories were not available unto 9 August - just two weeks prior to the start of classes. This significantly shortened set-up time than was expected required faculty members to spend considerable effort equipping and outfitting laboratories as well as setting-up, tuning and calibrating sensitive instrumentation so that all laboratory classes would be ready for a smooth start as the semester began.

Despite the unexpected activities associated with moving into the renovated facilities, twenty-six USNA Chemistry Department faculty members and an equal number of 1/C chemistry majors were able to carry out research on almost fifty different research projects. These included thirty-three sponsor-funded efforts covering a wide range of chemical and biochemical projects, from the synthesis of new potential pharmaceuticals, to molecular dynamic simulations of atomic level processes to detection of trace contaminants in the upper atmosphere. Funding agencies included the Air Force Office of Scientific Research (AFOSR), the Air Force Research Laboratory (AFRL), the Army Research Office (ARO), the DOD High Performance Computing Modernization Program, the DOD Strategic Environmental Research and Development Program, a General Electric Fellowship (administered via the University of Michigan), a Kinnear Fellowship, the National Aeronautic and Space Administration (NASA), the National Institute of Health (NIH), the National Science Foundation (NSF), the Naval Academy Research Council (NARC), the Naval Research Laboratory (NRL), the Naval Surface Warfare Center (Indian Head), the Office of Naval Research (ONR), Walter Reed Army Institute for Research (WRAIR) and the Research Corporation. The above efforts resulted in twenty publications, eight book chapters, and forty-four presentations, including several by midshipmen researchers at regional and national scientific society meetings.

Faculty members whose accomplishments are particularly noteworthy include Professor Judith Harrison who supports three full-time post-doctoral associates doing molecular dynamic simulations. This group produced three refereed journal articles, two book chapters and eleven presentations. Almost equally prolific was Associate Professor Paul Trulove who supports two full-time post-doctoral research associates (responsible for four refereed publications, three book chapters, a conference proceedings paper and six presentations), and Associate Professor Daniel O'Sullivan who produced two publications and seven scientific presentations. Assistant Professor Brian Rehill and Professor Graham Cheek each had two publications during the '04-'05 reporting period. Professor Cheek, as well as Professors Elert, Copper and Schroeder continued long and fruitful collaborations with the Naval Research Laboratory. New sources of funding include the NIH, the AFRL and the John and Aileen Crowley Bioscience Fund, a private donation intended to promote midshipmen education in the biosciences. Assistant Professors Tammy Domanski and Jamie Schlessman were selected as Crowley Bioscience Fellows and Associate Professor Joseph Urban was selected as a Kinnear Fellow.

Sponsored Research

Electrochemical Behavior of Titanium Chlorides in a Room-Temperature Ionic Liquid

Researcher: Professor Graham T. Cheek
Sponsors: United States Naval Academy Sabbatical and Naval Research Laboratory (NRL)

In a project designed to explore the electrochemical behavior of $TiCl_2$, $TiCl_3$, and $TiCl_4$ in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate. In this system, $TiCl_2$ was found to be insoluble, but dissolution of $TiCl_3$ and $TiCl_4$ gave well-defined cyclic voltammetric responses. For $TiCl_3$, a redox system involving the 3+ and 4+ oxidation states was observed at +0.3V vs Ag/AgCl, followed by a poorly-defined reduction process between -0.5 V and -1V. The latter process may involve reduction to the metallic state and may provide information in an ongoing effort to produce titanium metal from TiO_2. Addition of chloride ion to a $TiCl_3$ solution results in shift of the +3/+4 process to 0.0V, presumably by complexation of the titanium species by additional chloride ions. The voltammetric behavior of $TiCl_4$ is similar to that of $TiCl_3$, implying that the same +3/+4 couple is involved. Further experiments involving EXAFS are planned in an attempt to determine the coordination number of the titanium species, both regarding oxidation state and amount of added chloride.

Electrochemical Determination of Water in a Room Temperature Ionic Liquid

Researcher: Professor Graham T. Cheek
Sponsors: United States Naval Academy Sabbatical and Naval Research Laboratory (NRL)

This project involves the determination of water levels in the ionic liquids 1-ethyl-3-ethylimidazolium tetrafluoroborate (EMI BF_4) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMI BF_4). It has been found that addition of water to these ionic liquids produces cyclic voltammetric responses at -1.0 V (H_2O reduction), and +2.0V (H_2O oxidation), followed by a broad oxide reduction process between +0.5 V and -0.3 V vs Ag/AgCl. The response at +2.0V was found to be useful to at least 40 mM, while the reduction response at -1.0V reached a limiting current at 10 mM. This method is useful to ongoing work in these ionic liquids because it can be carried out in exactly the same solution to be used in a given investigation. It also avoids complications in the Karl Fischer method caused by interactions between tetrafluoroborate and the methanol used in the KF solution.

Production of Titanium from Titanium Dioxide

Researcher: Professor Graham T. Cheek
Sponsors: United States Naval Academy Sabbatical Program and Naval Research Laboratory (NRL)

In an ongoing project at the Naval Academy and the Naval Research Laboratory, the electrochemical behavior of TiO_2 is being investigated in room-temperature ionic liquids (RTILs). Using information gained from previous studies of titanium compounds in these laboratories, the conditions under which reduction of TiO_2 to titanium metal occurs is being explored. The importance of solution composition, especially regarding chloride, is the focus of present investigations.

Separation and Detection of Explosives by Capillary Electrophoresis

Researcher: Associate Professor Christine L. Copper
Sponsor: Dr. Greg E. Collins, Chemical Dynamics and Diagnostics Branch, Chemistry Division, Chemical Sensing/Chemometrics Section, Code 6112, NRL

Capillary electrophoresis (CE) is a separation method that has advantages of high efficiency, fast analysis time, small sample requirement, and minimal waste production when compared to other separation methods. This project centered on developing CE methods using sol gel chemistry to separate and detect explosives residues. Sol gels are permeable solid systems that can be generated in the CE separation capillary. These stationary phases can be created with various porosities and surface properties so as to alter the movement of molecules through the capillary based on the molecules' characteristics; thus causing the separation of different molecules (such as

explosives residues). Sol gels having various characteristics that influence CE separation of explosives residues were developed and tested. Several sol gel systems were found to give successful separation and detection of explosives such as TNT, RDX, HMX, etc. Conditions including buffer pH, separation voltage, buffer composition, and injection time were optimized. This project was started in May of 2004 and continued during the academic year in conjunction with NRL and with two midshipman research students.

Platinum-Free and Low-Platinum Nanocomposite Catalysts for Oxygen Reduction at Fuel Cell Cathodes

Researcher: Lieutenant Commander Gregory B. Cotten, USNR, Ph.D., P.E.
Sponsor: Naval Research Laboratory (NRL)

The development of new nanocomposite oxygen-reduction catalysts designed for high catalytic activity plus high electron and proton transport was investigated. With this approach, we anticipated that the oxygen-reduction reaction will be improved, increasing the efficiency of PEMFCs. Furthermore, the amount of platinum in fuel cell cathodes would be drastically reduced or eliminated, lowering the cost of the PEMFCs.

Reports have shown that Pt-Fe catalysts have up to 25 times the activity of Pt catalysts for oxygen reduction, and give weak evidence that this effect is due to a Pt-Fe alloy. Like the Pt-Ru system, it is likely that the active material is actually a nanocomposite of metals and oxides. Pt-Fe catalysts were used to resolve whether the active catalyst is a Pt-Fe alloy or Pt-FeOxHy composite. The stability of the Pt-Fe systems were also examined in the acidic and oxidizing conditions of the PEMFC cathode.

Platinum-free nanocomposite catalysts were synthesized with a focus on the optimization of catalytic activity plus proton and electron transport. For instance, phosphate-based materials, such as vanadium phosphorous oxide, were used to enhance oxygen activity. These catalysts are traditionally used for high temperature partial oxidation reactions due to their ability to abstract hydrogen and store oxygen in their lattice. Like many phosphates, vanadyl phosphates are good proton conductors, and often exhibit semiconduction. By mixing with metallic perovskites, such as CaMoO3 and SrCrO3, the conductivity of the electrodes will not be limited by electron transfer. The materials were evaluated for stability under acidic and oxidizing conditions.

These catalysts were provided to the DOE fuel cell testing facility at LANL for characterization under fuel-cell operating conditions.

Environmental Stress Response in *Staphylococcus aureus*

Researcher: Associate Professor Tammy L. Domanski
Sponsor: Naval Academy Research Council (NARC)

S. aureus is a major opportunistic pathogen that is the leading cause of nosocomial, hospital-acquired, infections. It has the capacity to cause infections ranging from mild skin infections to food poisoning, pneumonia, and Toxic Shock Syndrome.The focus of this project is to understand the infectious role of *S. aureus.* Toward that goal, two projects have developed. First, the potential role of ClpB in the *S. aureus* infection process and/or its ability to survive environmental stress conditions was studied. To determine the function of *S. aureus* ClpB *in vitro,* an *E. coli* strain defective in ClpB production has been utilized as a model system in which to study the heterologous expression of *S. aureus clpB*. While the strain, MC4100, obtained from another laboratory, was not found to exhibit the phenotype reported, RT-PCR analysis was useful in determining several conditions that induce *clpB* expression. Both high and low temperature shock increased the amount of *clpB* RNA in *S. aureus* cells. To study the function of the ClpB protein, the gene was cloned into an expression vector. Initial experiments indicate that ClpB protein is present in induced cells. Second, the emergence of *S. aureus* strains that are resistant to antibiotic treatment, and the current findings that infection is spread in communities and among athletes has lead to an epidemiological study of the strains of *S. aureus* isolated from clinic patients and the environment has begun as a Trident project (Midn 1/C Bowers) and continued over the summer months of 2004. Additional testing of outdoor fields indicated that neither natural or artificial turf act as reservoirs of *S. aureus*. The genomic data collected from the environmental and clinical strains obtained by Midn 1/C Daniel Bowers was further manipulated and analyzed for submission.

Molecular Dynamics Dimulations of Cubane Detonation

Researcher: Professor Mark L. Elert
Sponsor: Naval Research Laboratory (NRL), Code 6189

In recent years the AIREBO empirical bond-order potential, which allows accurate simulation of reactive chemical systems of hydrocarbons, has been used to model shock-induced chemistry in a variety of hydrocarbon molecular solids. In all cases studied so far, including the exothermic shock-induced polymerization of acetylene, there was not sufficient energy release from shock-induced chemical reactions to initiate sustained detonation. This year, molecular dynamics simulations of shock impact in the novel energetic material cubane were carried out, using a simplified cubic crystal unit cell geometry. For the first time in such simulations, self-sustained detonation was observed.

Antimalarial Chalcones

Researcher: Assistant Professor Clare E. Gutteridge
Sponsor: Walter Reed Army Institute of Research (WRAIR)

The ongoing investigation of substituted chalcones was continued; the aim being to identify compounds with good *in vitro* antimalarial activity and then test these for *in vivo* activity. One facet to the research was the development of a structure-activity model bringing together the results from the compounds made in FY03/04. This computational model provided a description of the structural requirements for active compounds in chalcones and related structures. It was used in the design of compounds to be prepared in FY06, and in the identification of new leads (including one to be pursued in FY06 in a Trident project). A second facet to the research was investigation of a chalcone described in the literature as being effective at curing mice infected with malaria, since this result is the basis for the potential of chalcones as antimalarials. The compound was prepared and tested for efficacy *in vivo* and found not to be active. It was postulated that metabolism of the parent compound contributed to this result; three metabolites were identified following exposure of the compound to metabolizing enzymes. Though one of these was partially curative *in vivo*, these results significantly reduced interest in the chalcones as an antimalarial lead. A third facet was an *in vivo* efficacy study of the best five chalcone inhibitors synthesized in FY04; all were found to be inactive. Again metabolism was proposed as the cause; the metabolic half-life of three of the compounds was subsequently tested and found to be very short. A search for a metabolically stable replacement led to the identification of a diphenyl-substituted, α-ethoxy amide. Studies in FY05 will focus such compounds since they match the structural requirements for active compounds delineated by the computational model.

MD Investigations of the Friction and Tribology of Solid Lubricants

Researchers: Assistant Research Professor David Schall and Professor Judith A. Harrison
Sponsor: Air Force Office of Scientific Research (AFOSR)

Microelectromechanical systems (MEMS) represent an emerging technology. These systems have generated a great deal of interest because of their potential use as sensors and actuators. The devices are on the order of microns in size and it is possible to fabricate thousands of devices at one time for a cost of a few cents per device. Consequently, systems with MEMS-based technologies will be lighter, smaller, and be less expensive than systems utilizing non-MEMS-based technologies. Workers at Sandia National Labs predict that these devices will play a significant role in future technologies with a broad range of commercial and military applications. Possible future applications of MEMS-based devices include accelerometers for use in military systems such as stability control, attitude heading reference, and short-time flight navigation. The use of silicon-based MEMS devices in nanosatellites to form an interconnected aerospace surveillance system has been proposed by The Aerospace Corporation. Workers at Hughes Aircraft Company and collaborators have proposed a MEMS-based system to replace current rocket, missile, and space vehicle navigational systems.

Silicon-based MEMS devices suffer from two major problems. First, because these devices are so small, the fabrication process can leave critical components adhered to one another. This phenomenon, call stiction, renders the MEMS device inoperable. Second, the wear rate of silicon is such that MEMS composed of silicon cannot be used in applications were parts are in relative motion for extended periods of time. To overcome these problems, researchers at the University of California have suggested coating the silicon-based MEMS with carbon

coatings. Researchers at the Raytheon Corporation have suggested constructing MEMS devices from diamond because it possesses superior friction and wear properties compared to silicon. We have extensive experience investigating the friction and wear of diamond, which should lend insight into the construction of diamond-based MEMS. In addition, we are currently debugging a molecular dynamics code that will be capable of examining the friction and wear properties of silicon-based MEMS devices coated with carbon films.

Classical molecular dynamics simulations have been conducted to investigate the atomic scale friction and wear when hydrogen-terminated diamond (111) counterfaces are in sliding contact with diamond (111) surfaces coated with amorphous carbon films, or diamond-like carbon films. A detailed analysis of the friction and wear of films with different sp^3-to-sp^2 carbon ratios was performed. In addition, films with large amounts of sp^3 carbon and hydrogen termination were also examined. The layered nature of both types of films was shown to influence the mechanical and tribological properties of the films. The nature of the carbon at the contacting interface was also shown to govern the tribochemical reactions that occurred between the counterface and the film. This work was published in the *Journal of Physical Chemistry B*. More recently, we have begun a systematic examination of the mechanical and tribological properties of amorphous carbon films doped with silicon and hydrogen. Preliminary results show that increasing the percentage of silicon in the films changes the mechanical properties of the film. A detailed analysis of the effects of percent silicon and temperature on the mechanical and tribological properties of these films is planned.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

Researchers: Assistant Research Professor Kevin Van Workum,
Assistant Professor Paul T. Mikulski (USNA Physics Department), and Professor Judith A. Harrison
Sponsor: Office of Naval Research (ONR)

Friction and the related phenomenon of wear are two of the more costly problems facing industry today. Understanding and ultimately controlling friction and wear has long been recognized as being central to many areas of technology. For instance, combustion engines break down and cutting tools become dull usually because of friction induced wear. Despite the obvious importance of friction and the induced wear, much of the atomic-scale dynamics responsible for these phenomena remain elusive. If the atomic-scale origins of friction and wear were understood, this might ultimately lead to the design of materials with specific friction and wear properties.

Molecular dynamics (MD) simulations are being used to investigate the atomic-scale origins of friction and wear in hydrocarbon systems. Using MD simulations has proven useful in examining atomic-scale friction and relating the results to experimental data. For example, tribochemical reactions and their atomic-scale mechanisms were cataloged. These reactions and their products were consistent with inferences drawn from macroscopic friction experiments on diamond.

Atomic force microscope (AFM) measurements have examined the friction of spiroalkanedithiols and a single structurally related normal alkanethiol chains bound to Au surfaces. Various surface science techniques were used to ascertain the order of the monolayers. These studies clearly show that the more ordered monolayer (more tightly packed) has lower friction measured with the AFM. In addition, films composed of chains of one length have much lower friction than monolayers composed of chains with different lengths. We have used our re-fit potential energy function to examine the friction of n-alkane chains on diamond. Two systems, one composed of pure C_{14} alkane chains (pure monolayer) and a second with a random, 50-50 mixture of C_{12} and C_{16} alkane chains (mixed monolayer) were examined. Contact forces between the amorphous carbon tip and the monolayers were examined in detail. The simulations showed that when sliding in the direction of chain tilt, the pure monolayer system exibited lower friction. Analysis of the contact forces at the interface revealed that there is an asymmetry between the forces that oppose tip motion and the forces that "push" the tip along in the mixed monolayer system that is not present in the pure monolayer system. Because friction can be defined as the sum of the forces opposing tip motion and the forces pushing the tip along the friction is high when there is an asymmetry between these forces. These results shed significant insight into the origin of the friction differences observed in the spiroalkanedithiol systems. This work was recently published in *The Journal of Chemical Physics.*

Multi-functional Extreme Environment Surfaces: Nanotribology for Air and Space

Researchers: Dr. Guangtu Gao, Professor Judith A. Harrison (Co-PI) and multiple Co-PIs elsewhere
Sponsor: Multi-University Research Initiative (MURI): AFOSR

Tribological issues such as friction and wear are currently the limiting factors in the development and commercialization of a myriad of enabling technologies for advanced air and space applications, with surfaces and lubricants frequently being the weakest link in overall system reliability and performance. While no single lubricant/coating has been identified that can withstand the entire range of extreme environments encountered by these systems, multi-functional nanocomposite materials appear capable of withstanding such debilitating tribological conditions. Their widespread implementation will be inhibited, if not impossible, however without tribological design rules that are integrated from the onset with system design. This project brings together an unparalleled team of experts with wide ranging backgrounds but one common goal: Solution of Air Force/DoD and commercial tribological problems deemed paramount, while concomitantly training personnel and collaborating closely with Air Force researchers to carry forth these solutions in DoD and industrialsettings.

The MURI team will (1) develop the scientific basis for tribological properties in terms of scale-dependent thermal, chemical, and mechanical processes that is critical for the engineering of advanced materials and coatings with tailor-made properties, and (2) from this basis introduce a new generation of coatings comprised of constituents that are optimally scaled and blended for life-cycle service in extreme environments associated with air, space and MEMS applications that would be of critical importance to the Air Force, DoD and industry. To accomplish these goals, our team will combine methods for synthesizing advanced materials, highly innovative and unique test-devices, and extensive multiscale modeling to identify and take advantage of critical physical mechanisms that underlie successful performance of structures for service in a widely varying range of extreme environments. This strong coupling between synthesis, testing, and modeling, which is a hallmark of our team, will provide unprecedented new insights and engineering capabilities that are not possible through individual efforts.

NIRT: Multi-Scale Modeling and Simulation of Adhesion, Nanotribology and Nanofluidics

Researchers: Dr. Mark O. Robbins, Jean-Francois Molinari, Shiyi Chen,
Dr. N. Bernstein, and Professor Judith A. Harrison
Sponsor: National Science Foundation (NSF) and The Johns Hopkins University

This Nanoscale Interdisciplinary Research Team's (NIRT) goal is to develop modeling techniques that can be used over a wide range of length scales to model adhesion, nanotribology, and nanofluidics. The team brings together experts in finite element (FE) analysis (Molinari and Chen), molecular dynamics (MD) (Robbins and Harrison), and in coupling these techniques (Bernstein). Coupling course-grained (FE) and atomistic-scale (MD) techniques should allow one to study problems such as adhesion over very long, e.g., nanometer, length scales. Results from these nanometer length-scale simulations should be directly comparable to experimental devices, such as, microelectromechanical systems. For the past academic year, Prof. Harrison has been working on this project at The Johns Hopkins University.

Electrochemical Studies of Photo-/Redox-Active Amylose Inclusion Complexes

Researcher: Associate Professor William B. Heuer
Sponsor: Naval Research Laboratory (NRL)

Amylose complexes of amphiphilic, *tris*(bipyridyl)ruthenium(II)–viologen (D-A) conjugates exhibiting intramolecular photoinduced electron-transfer quenching are being studied in order to correlate the electrochemical response of the included viologen acceptor with the electron-transfer properties. Previous results suggested significant changes in both the emission properties and electrochemical properties of the conjugates in DMSO-water mixtures are induced by the presence of amylose, though it was not possible to conclude with certainty that these changes are the result of inclusion. To address this question more definitively, studies have been undertaken to determine whether supramolecular inclusion of the viologen acceptor is accompanied by identifiable spectroscopic or electrochemical changes that might serve as a definite signal of inclusion.

Model viologens incorporating one long (C_8, C_{12} or C_{16}) and one short (C_1 or C_2) alkyl chain have been synthesized as halide salts, followed by counter ion exchange to the corresponding PF_6^- salt using $AgPF_6$ in acetone

and purification via column chromatography on silica gel. Preliminary electrochemical experiments on these model compounds suggest that the presence of amylose in solution substantially stabilizes the viologen radical cation formed upon electrochemical reduction. Upon admission of air to the solutions, the characteristic color of the radical cation is discharged, however the rate of color loss is much slower when amylose is present, indicating that interaction with amylose protects the viologen radical from oxidation. In order to investigate this effect more fully, spectroelectrochemical experiments on the model compounds are being conducted using a locally-constructed optically transparent thin layer electrode cell.

Preparation of a Radioligand for Study of the AMPA Receptor by Positron Emission Tomography (PET)

Researcher: Associate Professor Christopher M. Kinter

Sponsor: PET Radiopharmaceutical Science Section Molecular Imaging Branch, Division of Intramural Research Programs, National Institute of Mental Health, National Institutes of Health

AMPA receptors are one of the three major ionotropic glutamate receptors. These receptors mediate normal synaptic transmission along excitory pathways and participate in the modification of synaptic connection during development and changes in the efficiency of synaptic transmission throughout life. The excessive or inappropriate stimulation of these receptors can lead to neuronal death or loss by a process known as excitotoxicity. Excitotoxicity has been implicated in the pathophysiology of a number of neurological disorders and neurodegenerative conditions. Positron Emission Tomography (PET) gives researchers the ability to noninvasively measure neurotransmitter receptor densities and metabolic change in human subjects by making use of compounds labeled with positron emitting isotopes (carbon-11, fluorine-18, oxygen-15) The development of novel compounds for the study of the AMPA receptor by positron emission tomography (PET) has the potential to aid in the development of AMPA receptor-based therapies and the development of new neuroprotective agents. It is anticipated that delivery to the National Institute of Mental Health of a reasonable quantity of a suitable precursor for radiolabeled synthesis of a AMPA receptor ligand will occur during summer 2005.

Degradation of emergent and explosive contaminant compounds in natural waters

Researcher: Assistant Professor Dianne J. Luning-Prak

Sponsor: General Electric Fellowship and the University of Michigan

This research was done in conjunction with Professor Daniel W. O'Sullivan and researchers at the NRL, who are principal investigators for research project that is sponsored by the Strategic Environmental Research and Development Program.

Nitrogenous energetic compounds can enter and pollute the aquatic environment through the fallout of unexploded ordnance at shooting ranges and the corrosion of underwater unexploded ordnance (UXO) casings. The impact of this pollution source on the aquatic systems depends on the capacity of the aquatic system to transform (chemically or biologically) these pollutants into less harmful species. In marine systems, initial work with trinitrotoluene (TNT) suggests that it is photodegraded faster in marine systems than in freshwater systems (personal communication). Such observations are compound specific, however. The objective of this work is to quantify photodegradation rates of nitroaromatic compounds such as TNT, cyclotrimethylenentrinitramine (RDX), and cyclotetramethylenentetranitramine (HMX) under ambient light conditions using samples of varying salinity. Degradation products will be identified and quantified using various analytical techniques. From December 2004 to present, a method to analyze TNT using high pressure liquid chromatography has been developed. Photodegradation experiments will begin when a solar simulator arrives (Dr. O'Sullivan).

Development of a Fluorescence Assay for Inosine in Messenger RNA

Researcher: Assistant Professor Daniel P. Morse
Sponsor: Naval Academy Research Council (NARC)

Inosine in messenger RNA is produced by RNA editing enzymes called adenosine deaminases that act on RNA (ADARs). The purpose of this project is to develop a simple and rapid method to measure the total amount of inosine in cellular mRNA. If such a method were available, one could perform a number of experiments, not previously possible, that would provide new insights into ADAR biology. For example, one could monitor changes in the amount of inosine in small animals (such as flies or worms) grown under a variety of physiological conditions. Alternatively, one could measure the effects on inosine production of mutations that alter the expression of ADARs or ADAR targets.

The experimental approach will be to combine two well-established technologies to produce a fluorescence assay for inosine. The first technology, called SELEX, allows one to select RNA molecules from a randomized pool that bind tightly and specifically to almost any small molecule that one chooses. Such RNAs are called "aptamers". The second is "molecular beacon" technology. Molecular beacons are nucleic acids (RNA or DNA) that produce light (fluoresce) upon binding to other nucleic acids. Thus, it should be possible to produce an RNA molecule that fluoresces upon binding to inosine. If such an RNA were added, in excess, to a mixture of nucleotides, the intensity of the light produced, would be proportional to the amount of inosine in the mixture.

As a proof-of-principle experiment, RNAs with the antibiotic tobramyosin as the ligand were selected, and experiments with these two RNAs are being investigated tobramyosin "beacon-aptamers".

Examination of the Relationship between Photochemical Peroxide Production and Chromophoric Dissolved Organic Matter (CDOM) alteration in Chesapeake Bay Waters

Researcher: Associate Professor Daniel W. O'Sullivan
Sponsor: Office of Naval Research (ONR) and Naval Research Laboratory (NRL) Cooperative Agreement

The optical properties of surface seawater are impacted by the levels of chromophoric dissolved organic matter (CDOM). Photolysis of CDOM in surface waters leads to the destruction of the chromophore, potentially controlling the optical transparency of some surface waters. Coincident with the photolysis of CDOM is the production of a variety of oxygen radical species (OH, O_2^-, HO_2 and RO_2) in surface waters, which lead to peroxide formation. A series of laboratory photolysis experiments and field measurements were performed to examine the relationship between peroxide formation and CDOM optical property changes. For each of the photolysis experiments, the peroxide concentrations were determined and several parameters to characterize changes in chromophoric dissolved organic matter were measured on each of the samples. In all the experiments changes in the absorption spectra for CDOM, ($a_d[\lambda]$), were observed as well as changes in the synchronized fluorescence spectrum as a result of the irradiations. For some experiments samples were collected to characterize the change in dissolved organic carbon in the samples during the irradiation. Loss of absorbance or fluorescence indicated photobleaching of CDOM, while decrease in DOC indicated oxidation of DOC. These results were compared to production of peroxides. Our results suggest a substantial production of peroxides from waters containing abundant terriginous C (humic substances), supporting the assertion that photochemically-mediated oxidation of terriginous DOM is a significant mechanism for its removal in coastal waters. Quantum yield data for peroxide production were substantially different than for CDOM photobleaching for the same water samples. These results support the assertion that changes in optical properties and CDOM chemistry, while certainly being related, are separate processes, and that optical change in CDOM does not necessarily imply chemical change. Project work continues in cooperation with NRL, and has resulted in one presentation and one accepted paper this year.

Gas, Cloudwater, and Rain Hydrogen Peroxide and Methylhydroperoxide Measurements in RICO

Researchers: Associate Professor Daniel W. O'Sullivan, (Co-PI)
and Dr. Brian G. Heikes, (PI; University of Rhode Island)
Sponsor: National Science Foundation (NSF) Division of Physical Meteorology

The Rain in Cumulus over the Ocean Experiment (RICO) investigates trade wind cumulus clouds and the surrounding clear air to further understanding of shallow cumulus cloud microphysics and dynamics, larger-scale meteorological interactions, and climate forcing induced by cumulus cloud impacts on radiation and moisture budgets. The RICO field project involved an international team of investigators employing *in situ* observations, remote sensing, and theoretical models. RICO traced the atmospheric physics and chemistry of particle evolution, from haze aerosol, to cumulus cloud droplet formation, alteration by clear-cloud air mixing and photochemistry, through to "warm-rain" precipitation development. In our collaborative sub-project of RICO, *in situ* chemical observations of gaseous hydrogen peroxide and methylhydroperoxide were made in clear and cloudy air in the marine boundary layer and lower free troposphere using the NCAR C-130 airborne platform. Observations of aqueous hydrogen peroxide and methylhydroperoxide condensed upon cloud size and larger droplets were attempted using a counter-flow virtual impactor. The peroxides are integral to understanding and predicting the temporal evolution of aerosol sulfate, cloudwater sulfate, and cloud condensation nuclei activity. The peroxides are the leading oxidants of sulfur dioxide dissolved in atmospheric water and sulfur dioxide oxidation is the principle chemical process by which aerosol dry mass increases. The RICO (Lesser Antilles in winter 2004-05) photochemical environment was favorable to the formation of hydrogen peroxide and methylhydroperoxide. Sulfur dioxide was present from oceanic sulfur gas emissions, episodic volcanism, and long-range transport of anthropogenic emissions. USNA participated in the field measurement phase and continues to perform data analysis. In addition USNA provided the organic peroxide standards. Methylhydroperoxide is not commercially available and was synthesized, and purified at USNA. The field measurement phase was completed this year, and we provided high quality hydrogen peroxide and methylhydroperoxide measurements for all 25 research and transit flights on the NCAR C-130.

Measurement of Gas-Phase H_2O_2, CH_3OOH AND CH_2O on the DC-8 during INTEX-A

Researchers: Associate Professor Daniel W. O'Sullivan, (Co-PI)
and Dr. Brian G. Heikes, (PI; University of Rhode Island)
Sponsor: National Aeronautical and Space Administration (NASA), Global Tropospheric Chemistry Program

H_2O_2, CH_3OOH, and CH_2O are primary and secondary photochemical products of naturally and anthropogenically emitted pollutants. These gases are active in odd-Oxygen and odd-Hydrogen photochemistry as reservoir species, and hence sources, of stronger oxidants like HO, HO_2, CH_3OO. The latter two species, HO_2 and CH_3OO , along with NO are the necessary precursors for tropospheric O_3 production. The former species, HO, is a principal oxidant for most atmospheric material, controlling their transport time, distribution and deposition patterns. In the case of SO_2 (a primary precursor of aerosol sulfate), HO, H_2O_2, CH_3OOH, and CH_2O are all coupled to its oxidation through gas, aqueous, and heterogeneous reactions. Peroxide and CH_2O concentrations are dependent upon the chemical environment; volatile organic carbon compounds (VOC's), oxygenated volatile organic carbon compounds (OVOC's), nitrogen oxides, ozone, and water vapor. They are also dependent upon the meteorological environment; advection and mixing processes and history, temperature, pressure, cloud and precipitation processes and history, and ultra-violet light. These dependencies make them tracers of chemical reaction mechanisms and of meteorological transport phenomena. Peroxide and formaldehyde measurements were performed during the INTEX-A field program on all test and research flights on the NASA DC-8. The resulting data for hydrogen peroxide, methylhydroperoxide, and formaldehyde have been submitted to the NASA Tropospheric Chemistry program data archive. Data analysis continues for the field measurements for peroxy-acetic acid, these are the first observations of peroxy-acetic acid in the atmosphere. These data should be available to the science team in early May. Contingent upon additional funding, data analysis on this project will continue.

Biotic and Abiotic Attenuation of Nitrogenous Energetic Compounds (NEC) in Coastal Waters and Sediments

Researchers: Associate Professor Daniel W. O'Sullivan, Michael Montgomery (Project Leader at NRL-DC) and multiple other investigators representing multiple institutions
Sponsor: Strategic Environmental Research and Development Program (SERDP), DOD-Navy

This project was initiated through the SERDP program for the U.S. Navy to address clean-up and disposal procedures for underwater unexploded ordnance (UXO). UXO casings eventually breach and release NECs through mechanical stress, corrosion, and low-order remedial detonations. These compounds can remain intact in the sediment, dissolve into the overlying waters (dissolution), or bind to particles and resuspend into the overlying waters (phase transformation). Over time, various chemical, biological, and physical processes (for example sequestration, metabolism and photolysis) change the NEC to other chemical forms that have different transport and toxicity properties in various ecosystems. Although SERDP has sponsored much work on NEC transformation in terrestrial and groundwater systems, very little information is available on rates of attenuation or transport of energetics in coastal aquatic systems. In lieu of evidence that these materials are rapidly degraded to nontoxic substances or metabolized by microbial assemblages, the Department of Defense (DoD) is being pressured to recover all UXO from coastal waters. Recent experimental work by the PI's has indicated that biodegradation and photodegradation rates of 2,4,6-trinitrotoluene (TNT) in marine waters are surprisingly rapid in comparison to their degradation rates in terrestrial environments. If confirmed, this information may help DoD remain in compliance with environmental regulations at critical operational ranges, and reduce UXO recovery and sediment clean up costs. The USNA component of the multi-institution SERDP project is directed at developing a quantitative understanding of the photochemical degradation rates of NECs (TNT, HMX and RDX) in marine systems. Laboratory experiments will be conducted to determine the photolysis rates in marine waters and to identify the degradation products.

Extent and Biological Impact of Chemical Variation within the Canopies of Riparian Trees

Researcher: Assistant Professor Brian J. Rehill
Sponsor: Naval Academy Research Council (NARC)

Plant chemistry frequently mediates ecological interactions. Biologists, geneticists, and ecologists understand that chemical variation within a population of plants affects the survival and reproduction of the animals that eat them, as well as the other organisms - predators, parasites, and mutualists - that comprise the associated community. However, much less understood is the way in which variation *within* an individual plant affects important ecological interactions. This continuing project aims to examine and extend the concept of developmentally based variation in phytochemistry as an ecologically important phenomenon, working in multiple systems.

The summer 2004 research period was used primarily to begin the work described in last year's proposal. Numerous local facilities were visited to assess their suitability for leaf collection and future research, such as Patapsco Valley State Park, Elk Neck State Park, and Severn Run Natural Area. Ultimately, Patuxent Research Refuge, managed by the U.S. Fish and Wildlife Service, was chosen as the site with the greatest initial potential based on forest species composition, access, and size. Permission to sample leaves was requested in a proposal and granted by Holliday Obrecht, Director of Research at the Refuge.

Leaf collection was delayed due to a lack of equipment (pole pruner and extensions) until September. Collection in September was extensive, and chemical analysis of leaf material will continue throughout the winter as part of several faculty-midshipman research projects. Collections were made from three tree species which dominate various portions of the lowland and riparian forests of Patuxent Research Refuge. These were: tulip poplar (*Liriodendron tulipifera*), sweetgum (*Liquidambar styraciflua*), and sycamore (*Platanus occidentalis*). Collections were done to test the hypothesis of developmentally based variation in phytochemistry in all three species, as well as to determine the extent of population-level variation in phytochemistry.

Further information about the projects is contained under the description of the Midshipmen 1/C Rusthoven and 1/C Vigilante research projects.

Accommodation of Electrostatic Charge within Proteins: Crystallographic Studies of *Staphylococcus Nuclease* Mutants

Researcher: Assistant Professor Jamie L. Schlessman
Sponsors: Dr. Bertrand Garcia-Moreno, The Johns Hopkins University Biophysics Department
and a National Science Foundation (NSF) Research Opportunity Award

The thermodynamics of protein stability involved a complex set of interactions between protein and solvent and within the protein itself. Traditional explanations for protein stability rely of entropic considerations in which hydrophobic amino acids are separated from the polar solvent (water) by burying them in the protein core. Introduction of an electrostatic charge within the protein interior destabilizes the protein and may lead to protein unfolding. However, charges form and are transferred within a protein's interior in numerous biochemical processes including catalysis, electron transport, and proton transfer, so a more nuanced explanation of charge accommodation is needed. X-ray crystallographic methods have been used to determine the structures for a number of mutants of Staphylococcal nuclease into which a destabilizing electrostatic charge (lysine (+) or glutamic acid (-)) had been introduced by mutation. These preliminary results showed an array of accommodation methods by the protein, including water penetration into the protein core, localized protein unfolding and, in a few cases, domain swapping between neighboring protein molecules. Recent work (Schlessman, J. L., Isom, D., and Garcia-Moreno E., B., unpublished) of the nuclease PHS/L38K mutant identified a novel internal salt bridge as a mechanism for charge accommodation. Additional protein structure determinations are underway to confirm these mechanisms and identify new mechanisms in other mutants, and to correlate structural findings with spectroscopic characterization of pKa shifts of the mutated residues. In a related project, the effects of distant mutations on internal histidine side chain conformations have been studied crystallographically. One structure has been completed for nuclease VIAGAN/E75A (Baran, K., Fitch, C., Schlessman, J, Garcia-Moreno, E. B., manuscript in preparation), and crystals for several other mutants have been obtained.

Relaxation Studies of Polymeric Glass-Formers

Researcher: Associate Professor Maria J. Schroeder
Sponsor: Dr. C. M. Roland, Naval Research Laboratory (NRL) Chemistry Division

Substances having diverse chemical structures vitrify, with the glass transition phenomenon characterized by dynamic and thermodynamic properties shared by all glass-formers. Fundamental understanding of the glass transition requires examination of the dynamics that precede it since these serve as precursors to structural relaxation. The existence of the Johari-Goldstein (JG) relaxation has long been considered universal in glass-formers. Caged dynamics in the form of the nearly constant loss (NCL) has also been regarded as a general property of glass-formers. However, few studies have been conducted on polymeric glass-formers in these high-frequency regions. Recently, the existence of the JG relaxation and NCL behavior was confirmed in 1,4-polyisoprene (by this researcher and coworkers). In this work, other polymeric glass-formers, polybutadiene, polydimethylsiloxane, and polyphenylmethylsiloxane, for which neither the JG relaxation nor the NCL have been reported previously, were studied by employing a high resolution capacitance bridge under optimal conditions. Analysis of the dielectric relaxation behavior and the temperature dependences of the JG relaxation time and NCL will be conducted in hopes of comparing them to theoretical predications, and providing a basis for understanding glass transition behavior.

Synthesis and Characterization of New Polycarbonate Materials for Impact Protection

Researcher: Associate Professor Maria J. Schroeder
Associate Professor John T. Bendler (USNA Physics Department)
Sponsors: Department of Defense (DoD) and U.S. Army Research Office (ARO)

The U.S. Army is currently investigating the development of new synthetic polymers and nanocomposites for use in transparent armor and coatings applications. Novel synthesis procedures have been developed for a number of polymer systems based on polycarbonate materials. Polycarbonates have long been used in engineering applications because of their optical transparency and strength. With the aid of molecular modeling, these new polycarbonate-based materials have been designed to provide greater impact resistance, processability, heat resistance, and chemical stability over the current materials. Characterization studies of the new materials have

included thermal analysis by differential scanning calorimetry (DSC), and molecular weight determinations by gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). The goals of this project include synthesis and characterization of these new polymeric materials in hopes of determining the origin of their enhanced properties and advancing the development of high-performance materials for military applications.

Structural Investigation of the Ligand-binding Properties of the Chaperone Protein SecB of *Escherichia coli*

Researcher**:** Assistant Professor Virginia F. Smith
Sponsor**:** Dr. Linda L. Randall, Department of Biochemistry, University of Missouri-Columbia

Chaperone proteins are a general class of proteins that perform a vital function in the cell by preventing improper interactions between proteins that might lead to degradation and aggregation. Many of these chaperone proteins work according to relatively well-understood mechanisms that require cleavage of the chemical energy molecule adenosine triphosphate (ATP). However, less is known about the chaperone protein SecB of *Escherichia coli*, which does not require ATP in order to perform its job. We exploited our knowledge of the three-dimensional structure of SecB to obtain information about the mechanism by which SecB recognizes the proteins it binds to and determine how it prevents them from aggregating or becoming degraded. Using chemical crosslinking and high-resolution separation techniques, we investigated the ligand-binding mechanism of SecB in order to obtain a detailed picture of the protein-protein interactions that confer protection.

Enzymatic Repair of Proteins Damaged by Oxidation

Researcher: Assistant Professor Virginia F. Smith
Sponsor: Cottrell College Science Awards, Research Corporation, Tucson, AZ

Although oxygen is essential for life, too much oxygen can be disastrous. Modification of proteins, DNA and lipid molecules by certain oxygen-containing molecules (*e.g.,* superoxide, hydrogen peroxide, the hydroxyl ion, and water) has been shown to contribute to human disease and the aging process. Although most of these changes are irreversible, certain modifications can be repaired by enzymes present in our body. One such repair enzyme is methionine sulfoxide reductase (MsrA). Although MsrA is an essential protein – it has been found in the genome of every organism sequenced to date – we are just beginning to understand how it works. In this project, protein folding methods are used to answer fundamental questions about MsrA and biological oxidation by observing how this interesting enzyme folds to its three-dimensional form, how it recognizes damaged proteins and how it then repairs them.

Development and Characterization of Advanced Dual Intercalating Molten Electrolyte Battery Systems

Researchers: Assistant Professor Paul C. Trulove,
Dr. Hugh C. De Long (AFOSR) and Assistant Research Professor Wesley A. Henderson (USNA)
Sponsor: Naval Research Laboratory (NRL)

Room-temperature ionic liquids composed of perfluoroanions and nitrogen based organic cations possess a number of unique properties that make them ideal electrolytes for compact power sources. In particular, they are nonflammable, nonvolatile, and chemically inert, and they display wide electrochemical windows, high inherent conductivities, and wide thermal operating ranges. Also, unlike room-temperature ionic liquids based on chloroaluminate anions, these perfluoroanion electrolytes are not moisture sensitive.

For manufacturing and design optimization, solid-state electrolytes with high ionic conductivities are preferred to liquid electrolytes. In this research program we are investigating the generation of solid-state electrolytes that incorporate perfluoroanion ionic liquids into a poly(vinylidene fluoride)-hexafluoropropylene copolymer. These free-standing rubbery electrolytes appear to retain much of the desirable properties of the perfluoroanion ionic liquids. In this project we will be investigating the physical and electrochemical properties of these gel electrolytes using thermal mechanical analysis, differential scanning calorimetry, imbedded microelectrode

techniques, AC-impedance, and luminescent probe molecules. In addition, this project will evaluate graphite intercalation anodes and cathodes with the ionic liquid-polymer gel electrolytes in solid-state cells employing the dual intercalating molten electrolyte (DIME) concept.

Conductive Nanocomposites as Indium Tin Oxide Replacements

Researcher: Assistant Professor Paul C. Trulove,
Dr. Hugh C. De Long (AFOSR), Dr. Jeffery W. Gilman (National Institute of Standards and Technology),
Dr. Robert A. Mantz (Air Force Research Laboratory (AFRL),
and Assistant Research Professor Douglas M. Fox (USNA)
Sponsor: Air Force Research Laboratory (AFRL)

Conductive nanocomposite materials represent a potential replacement to indium tin oxide (ITO) in low observable applications. These composite materials would not only replace the ITO that is currently used but would integrate the conductive material directly into the composite so the conductive element would not be a thin coating on an exterior surface were it is prone to damage. Recent work by our group has identified a unique method to disperse and compatibilize carbon nanotubes with organic polymers. We are now investigating the potential of generating conductive nanocomposite materials using carbon nanotubes as the high aspect ratio conductive element. To date many groups have attempted to disperse and compatibilize nanotubes in various polymers with limited success. If carbon nanotubes were effectively dispersed in a nanocomposite they should reach their percolation threshold at low filler concentration due to the high aspect ratio of the nanotubes. Our group has already show that the use of ionic liquids as dispersant / compatibilizer can generate high-quality carbon nanotube nanocomposites with polystyrene. We are currently working to extend this work to important engineering polymers such as polycarbonate. We are working to thoroughly characterize the interplay of ionic liquid treatment and processing conditions in order to maximize electrical conductivity through effective dispersion and compatibilization while simultaneously minimizing carbon nanotube loading.

Biopolymer Nanocomposites

Researcher: Assistant Professor Paul C. Trulove,
Dr. Hugh C. De Long (AFOSR), Dr. Jeffery W. Gilman (NIST), Dr. Robert A. Mantz (AFRL),
Assistant Research Professor Douglas M. Fox (USNA),
Assistant Research Professor Wesley A. Henderson (USNA) and Dr. Paul Maupin (Department of Energy)
Sponsor: Air Force Office of Sponsored Research (AFOSR)

Although a material of ancient origin, silk has properties that rival many of our most advanced synthetic polymers. Much effort has gone into exploiting the properties of silk in composite materials, but success has been limited due primarily to our inability to reliably dissolve and reconstitute silk proteins. Ionic liquids represent a unique class of solvents that offer unprecedented versatility and tunability. Recent work has shown the potential of ionic liquids as solvents for the processing of biopolymers. In addition, ionic liquids have recently been shown to significantly enhance the interaction of nano-scale clays and carbon nanotubes with polymeric materials. In the proposed research we will investigate the dissolution and reconstitution of silk and related biopolymers (e.g., collagen, elastin, chitin) in and from ionic liquids; we will use ionic liquids to prepare silk composite materials that incorporate nano-scale layered silicates and carbon nanotubes; and we will employ a variety of methods to evaluate the macroscopic and microscopic properties of these unique biopolymer nanocomposite materials.

Conformational Analysis: The Role of Stereoelectronic Effects

Researcher: Associate Professor Joseph J. Urban
Sponsor: DoD High Performance Computing Modernization Program

This ongoing research is focused on using computational chemistry techniques to study the fundamental intermolecular and intramolecular interactions that determine a molecule's conformational preferences. Molecular conformational preferences can play a major role in a variety of chemical, physical, and biological properties. The conformational distribution exhibited by a molecule under a given set of conditions represents a balance between the

intramolecular interactions between the constituents of the molecule itself and the intermolecular interactions with the surrounding environment (solvent for example). For all but the simplest molecular systems, the energy differences between conformations are difficult, if not impossible, to measure experimentally. Thus, computational studies are often the only source of quantitative data for many systems of interest. The lack of available experimental data to calibrate approximate computational methods (molecular mechanics force fields), and the fact that the energy differences between conformations are typically very small makes it necessary to employ very high levels of theory, which requires the use of high performance computing resources. One of the specific goals of this work is to examine the effect of fluorination on the conformational preferences of model compounds and to evaluate the performance of a variety of computational methods in describing these effects. For a series of alkylamines, subtle stereoelectronic effects were seen to play a major role in determining the conformational preferences in fluorinated and trifluorinated compounds. However, in the alanyl didpeptide, fluorination in the beta position does not result in drastic changes in the backbone conformational preferences.

Natural Product Antifouling Coatings Based on the Controlled Delivery of Biofouling Repellents

Researchers: Mr.Ronald R. Price and Lieutenant Eric R. Welsh, USNR, Ph.D.
Sponsor: Naval Research Laboratory (NRL)

The scope of this research is to design and develop antifouling coatings that use an active agent derived from seaweed in a controlled-release system composed of an entrapping agent and a bio-derived polymer with adjustable degradation properties.

Significant progress has been made in the scale-up and synthesis of the active agents, known as furanones, polymer (chitosan), and a cross-linker. Studies on the developed coating systems have yielded five peer-reviewed publications: two in Biomacromolecules; one in Carbohydrate Polymers, which derived from a collaborative effort with researchers at NIST on chitosan hydrogels; one in Langmuir; and one in the Journal of Microencapsulation. Furthermore, one patent application (Navy Case No: 96,826) has been filed for this research.

New Approaches to Organic Materials for Photovoltaic Applications

Researcher: Associate Professor Craig M. Whitaker
Sponsors: Office of Naval Research (ONR),
Naval Research Laboratory (Dr. Brett Martin, Center for BioMaterials Science and Engineering),
and 2004 Kinnear Fellowship

This project's ultimate goal was the synthesis and characterization of organic-based photovoltaic devices. During the Summer of 2004, the research focused on the synthesis and characterization of novel, organic photovoltaic (PV) materials with the intent of creating a highly efficient PV device. A molecular composite of an oligo(phenylenevinylene) (OPV) light harvesting unit and an electron-conducting hydroxylated 3,4-ethylenedioxythiophene (EDOT-CH_2OH) unit was created. The molecular composite's conductivities and optical transparencies were tested at the Naval Research Laboratory. The information gathered from the experimentation and analysis will help develop an understanding of how molecular composites can be employed to create useful organic photovoltaic devices.

Due to funding issues in August 2004, the research emphasis for this project changed, but the collaboration with Dr. Brett Martin at the Naval Research Laboratory continued. The main objective of the project for the Fall 2004 semester was the synthesis and characterization of hydroxylated 3,4-ethylenedioxythiophene (EDOT-CH_2OH) monomer for the demonstration of reversible control of kinesin activity using the two different doping states of the conducting polymer as a support. The protein ensemble (streptavidin, BSA, Drosophila kinesin K401-biotin carboxyl carrier protein (BCCP)-His6 and microtubules) was deposited onto the conducting polymer surface (initially doped) using standard flow or droplet deposition methods. When the conducting polymer was electro-chemically cycled to their dedoped state the kinesin activity and microtubule speeds were measured. When the polymer is in its doped state, the ATPase activity of a dimeric kinesin derivative from Drosophila and the dependent microtubule speeds are ca. 44% of the theoretical maximum. When the polymer is electrochemically cycled to its

dedoped state the kinesin activity and microtubule speeds increase to ca. 70% of the theoretical maximum. This is the first example of an electrically switchable surface capable of moderating enzyme activity in this manner.

Functionalizing Single-Walled Carbon Nanotubes for Energetic Materials

Researcher: Associate Professor Craig M. Whitaker
Sponsor: Naval Surface Warfare Center, Indian Head Division (NSWC-IH)

The purpose of this research is to develop a new method for the creation of functionalized single-walled carbon nanotubes (SWNTs) for novel energetic materials. The functionalized carbon nanotubes will be incorporated or bound into propellant matrices for various possible energetic applications. The goal is to significantly enhance the initiation, overall propellant performance, safety, as well as in mechanical properties. Our first target molecule is a nitro group functionalized SWNTs that will be synthesize through Curtius Rearrangement of an isocyanate followed by oxidation of the primary amine. During the Spring 2005 semester, the SWNTs were purified, oxidized and characterized by IR spectroscopy to produce carboxylic acid functionalized SWNTs. The number of acidic sites on the SWNT-COOH were determined by titration analysis.

Independent Research

Synthesis of NMR Characterization of Derivatives of Menthol

Researchers: Associate Professor Debra K. Dillner
and Dr. Daniel Traficante, Naval Academy Preparatory School (NAPS)

Menthol is a naturally occurring terpene, often used as a chiral starting material or as a precursor to chiral auxiliaries. Previously, Breitmaier had synthesized menthane carboxylic acid, with the carboxylic acid group in the equatorial position. He made preliminary Nuclear Magnetic Resonance (NMR) assignments of its resonances. This project examined that structural assignment in greater detail, using additional 1D and 2D NMR techniques. In addition, several previously unknown menthol derivatives were prepared with substituents in the same position but located axially to the ring. Complete NMR spectral assignments of these derivatives were also conducted. These compounds are of interest, not only for their spectral properties, but also as precursors to chiral auxilaries complementary to those already available from menthol. The spectral characterization of these compounds has been completed and optimization of the synthetic pathway is underway.

Spectroscopic Studies of Thermal and Radiation Effects on Water-Ammonia Ices

Researcher: Professor Robert F. Ferrante

Water- and ammonia-ices have been observed or postulated as important components of the icy surfaces of planetary satellites in the outer solar system, such as Pluto and its moon Charon. Significant gaps exist in our knowledge of the spectra and behavior of such mixtures under astrophysical conditions of temperature, pressure and radiation environment. Laboratory studies provide necessary data to assist in interpreting and modeling the composition and thermal- and radiation-processing histories of such objects. Samples of water/ammonia ices were prepared by direct deposition of pure gases or gas mixtures of ammonia and water onto a low-temperature surface maintained by a closed-cycle helium refrigerator. The resulting ices were examined by low temperature (10 K - 160 K) FT-IR spectroscopy before and after thermal processing (accomplished by warming the samples to various temperatures appropriate for the astrophysical systems) or radiation processing (achieved by exposing the samples to a beam of 1 MeV protons generated by a van de Graaff accelerator). Changes in the spectra were indicative of formation or destruction of chemical compounds, or phase changes of the components. The experiments were mainly focused on two stable hydrates of ammonia, NH_3:H_2O and $2NH_3$:H_2O, and the effects of initial gas composition, deposition temperature, thermal- and radiation-processing on the spectra. Special emphasis was placed on the near-IR region, which is most accessible to ground-based observations, and in which less data is currently available. New features in the near-IR were reported for the two hydrates, and short-term radiation effects, modeling up to a few million years of solar system irradiation, were quantified for the first time. Early results were reported at the 227th National Meeting of the American Chemical Society in Anaheim in March 2004, with

additional results quantifying some long-term radiation effects reported at the COSPAR meeting in Paris France (July 2004, invited presentation) and the DPS meeting in Louisville KY (November 2004). Additional work examined the spectroscopy and behavior of non-stoichiometric mixtures and their tendencies to form the stable hydrate compounds in varied temperature regimes. Work is continuing on formation of the elusive third stable hydrate (NH_3:$2H_2O$), which may be important in terrains with relatively higher amounts of water. A summary manuscript on the entire system is in preparation.

Molecular Dynamics Simulations of the Bending of Filled Carbon Nanotubes

Researchers: Professor Judith A. Harrison, Assistant Professor Paul Mikulski (USNA Physics Department), Dr. Susan Sinnott and Dr. Boris Ni (University of Florida)
Heather Trotter, R. Phillips, and Dr. Yanhong Yu

The overall goal of this project is to examine the mechanical properties of carbon nanotubes. Nanotubes are filled with CH_4, C_{60}, and Ne. Mechanical properties as a function of filling gas, tube length, and temperature have been examined. This collaboration resulted in a publication in the *Journal of Nanoscience and Nanotechnology*.

Investigations into the Effects of Tripodal Ligands on Transition Metal Environments

Researcher: Associate Professor JudithAnn R. Hartman

The design of pre-organized ligands has been a major area of coordination chemistry for the last 40 years. Crown and cryptand designs have been successfully used to influence both ligand selectivity and the electronic environment of the complexed metal ions. However, it is unclear how much of the ligand effects are due to the cyclic or cage structures and how much to the pattern of linked chelant rings.

The properties of TREN-based podands to design an easily synthesized "pre-organized" ligand have been explored. Initial work has involved the study of aminopyridyl tripodal and linear ligands. In this study, the work has been expanded to include the "softer" aminothiophene ligands.

The following series of aminothiophene ligands have been synthesized and characterized: TREN-thio (tris(2-((2-thiophene)amino)ethyl)amine), EN-thio (1,7-bis(2-thiophene)-2,6-diazaheptane), DIEN-thio (1,9-bis(2-thiophene)-2,5,8-triazanonane), TRIEN-thio (1,12-bis(2-thiophene)-2,5,8,11-tetraazadodecane), and DIPNEN-thio (1,14-bis(2-thiophene)-2,6,9,13-tetraazatetradecane).

Work to synthesize and characterize the Ni(II) and Cu(II) complexes of these ligands is continuing. In addition, the thiophene ligand (made from diaminocyclohexane) is being synthesized.

Ignition Studies of Cerium Nitrate Treated Towels

Researcher: Associate Professor JudithAnn R. Hartman

Cerium Nitrate soaked towels are used by DOE in the process of decommissioning weapons production facilities. As a result of a recent fire, there is interest in the self-heating properties of cerium nitrate soaked rags that have not been properly decontaminated. The self-heating properties of these rags in a self-heating oven test are being studied with a group of coworkers at Hughes Associates. This work has resulted in a publication and the project is being continued with students at the Naval Academy. The midshipmen are studying the ability of laboratory methods to predict the self heating results from the larger scale, more time-consuming heating tests.

Novel Ligands for Surface Functionalization of Titanium Dioxide

Researcher: Associate Professor William B. Heuer

Currently, there is great interest in the use of metal complexes of α-diimine ligands (2,2'-bipyridine and analogues) as sensitizers in semiconductor-based photovolatic cells. Ruthenium(II) complexes typically make the best sensitizers, owing to their long-lived triplet MLCT excited state, which ensures efficient electron injection into the semiconductor substrate (typically TiO_2). Corresponding Iron(II) complexes likewise might exhibit temperature-dependent spin-transitions that may be useful in probing the dynamics of interfacial electron transfer at the semiconductor surface. In order to function as an effective sensitizer, the complex must be covalently attached to the surface. This can be achieved through use of functionalized α-diimine ligands bearing carboxlate or phosphonate groups, which are known to bind strongly to TiO_2 films.

As part of the initial phase of a collaborative project with Prof. Gerald Meyer of the The Johns Hopkins University Chemistry Department, the synthesis of some new types of functionalized α-dimmine ligands derived from 4,5-diaazafluoreneone (1), 1,10-phenanthroline-5,6-dione (2), and 1,10-phenanthroline-5,6-diamine (3) have been undertaken. Presently, condensation reactions between the ketone group of (1) and active methylene compounds (benzyl- or cyanomethylene derivatives) incorporating either carboxylate or phosphonate ester groups are being investigated. Using established chemistry, a plan exists to convert (2) and (3) into similarly-functionalized imidazo-phenanathroline and dipyridopyrazine derivatives, respectively. Following their preparation, these ligands will be used to synthesize new families of Fe(II) and Ru(II) complexes, the photophysical properties of which will be studied both in solution and when adsorbed onto the surface of nanoporous TiO_2 films.

Synthesis Of Polythiophene-Containing Block Copolymers From Ring-Opening Metathesis of Cyclobutenediones

Researcher: Assistant Professor Shirley Lin

One of the challenges of polymer chemistry is the synthesis of new, multifunctional materials with desirable properties. The properties of many homopolymers, polymers composed of a single type of monomer unit, are known. One way to create multifunctional polymers is through the selective combination of different monomers. Recently, the development of block copolymers, polymers in which one segment, composed of only one monomer, is attached to another segment composed of another monomer, has led to a wealth of materials with multiple desirable properties.

This project involves a new synthetic route to block copolymers containing poly(thiophene), an electrically conductive polymer useful in the fabrication of molecular electronic and optical devices. Unlike conventional syntheses of block copolymers containing poly(thiophene), which involve more than one polymerization method, we propose to create the thiophene units through post-polymerization modification of another polymer. Specifically, we propose to investigate the ring-opening metathesis polymerization (ROMP) of a highly-strained monomer, cyclobutenedione, that would result in a polymer containing 1,4-carbonyl functionality capable of cyclization into thiophene units. Given the versatility of recently developed ROMP catalysts, this route to block copolymers containing poly(thiophene) should lead to the development of entirely novel materials.

Results and Status: Several syntheses of cyclobutenedione, the target monomer for polymerization, have been investigated. Two promising syntheses are currently being pursued. Purchase of a nitrogen dry box is currently underway in preparation for investigating the polymerization reaction.

Organic Small Molecule Additives for the Crystallization of Proteins

Researchers: Assistant Professor Shirley Lin and Assistant Professor Jamie L. Schlessman

The study of protein structure has been an important component of biochemistry for the last fifty years. One method to obtain a protein's structure is to crystallize the protein and have a good quality crystal for X-ray diffraction. 2-methyl-2,4-pentanediol (MPD) is the most frequently used small organic molecule additive in the crystallization of proteins. Few other small molecules have been tested in the crystallization of proteins, with none

having greater success than MPD. This project is designed to identify alternative additives to MPD using egg-white lysozyme as the target protein.

Results and status: Five organic compounds were screened in the crystallization of lysozyme: 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,6-hexanediol, 1,2,6-hexanetriol, and β-cyclodextrin. Some crystals were obtained using 1,6-hexanediol in Spring 2004. These results have been reproducible but an x-ray diffraction quality crystal has not yet resulted. During Summer 2005, efforts to obtain a high-quality lysozyme crystal using 1,6-hexanediol will continue. Other small molecules will be investigated as additives. Other potential additives, such as polyelectrolytes and ionic liquids, have been identified.

Laser Lab Set Up & Completion of the manuscript "A Kinetic Study of the Reactions of Vanadium, Iron, and Cobalt with Sulfur Dioxide"

Researcher: Associate Professor Roy E. McClean

The laser lab is currently being set up for gas phase reaction kinetic studies. A laser photolysis / laser-induced fluorescence technique will be used for the investigations. Two laser systems have been installed, as well as parts of the reaction chamber and flow systems. Major work that still needs to be completed:

- slight modification of the laser system installation
- flow system completion
- interfacing of computer systems to lasers and other electronic equipment
- set up of data collection instruments (PMT, optics, etc.)
- modification of computer codes

The manuscript entitled "A Kinetic Study of the Reactions of Vanadium, Iron, and Cobalt with Sulfur Dioxide" was accepted by the *Physical Chemistry Chemical Physics*. In brief, it describes the chemical kinetic studies and density functional theory calculations on the V, Fe, and Co + SO_2 systems.

RNA Editing Targets in Mouse Embryos and Hematopoietic Stem Cells

Researcher: Assistant Professor Daniel P. Morse

Inosine in messenger RNA is produced by RNA editing enzymes called adenosine deaminases that act on RNA (ADARs). In mammals there are at least two ADARs called ADAR1 and ADAR2. Inactivation of the gene encoding mouse ADAR1 results in embryonic death by day 11 after fertilization. Death is due to wide-spread apoptosis (programmed cell death) and a failure to produce mature red blood cells. To further understand the biological roles of ADARs, this project aims to identify RNA editing targets that are responsible for the ADAR1-knockout phenotypes.

Previously developed methods for identifying inosine-containing RNAs are being used to find ADAR substrates in RNA isolated from mouse embryos and hematopoietic stem cells. Stem-cells are currently being grown by David Trisler at the University of Maryland, School of Medicine.

High-Pressure Crystal Structure of RDX

Researchers: Associate Professor Wayne H. Pearson,
and Dr. Suhithi M. Peiris, Naval Surface Warfare Center - Indian Head Division (NSWC-IH)

Although the crystal structure of the explosive, RDX, has been determined at room temperature and pressure, there is essentially no information concerning structural changes that occur to the explosive at high pressure. This project, which is in the preliminary stages, is an attempt to determine the high pressure (> 1 GPa) crystal structure of RDX. Preliminary synchrotron data were provided from Dr. Peiris at Indian Head. The data had been obtained using a diamond anvil cell with X-ray radiation at approximately 0.30 Angstroms. A structure solution was obtained for these data and a model, with isotropic temperature factors, was refined to an R(F) = 17%.

In spite of the uncertainty in unit cell measurements and a total lack of an absorption correction for the diamond anvil, this was a very favorable result. A full set of bond distances and angles were generated for analysis by the group at Indian Head. Additional attempts have been made to process the 2 Gpa and 3.5 Gpa datasets.

Progress over the summer months led to the successful installation of the Cornell DPS suite of software for analysis of the image plate frames. The Cornell software was not capable of indexing the frames. A more complete analysis of the patterns by examining spot positions and correlating with predicted positions led us to believe that the crystals were either twinned or had undergone a partial phase transformation. An attempt will be made to convert the existing images to frames that can be read by the new Bruker software that has been purchased as part of the new X-ray diffractometer procurement. This new software is optimized for small molecule data and is capable of analyzing twins.

Development of Novel Protein Crystallization Agents

Researchers: Assistant Professor Jamie L. Schlessman and Assistant Professor Shirley Lin

Crystallization is a requisite for X-ray structure determination for any protein. Obtaining a single crystal suitable for high-resolution diffraction studies remains a rate-limiting factor in protein structure determination, as crystallization conditions must be determined empirically for each protein sample. A common crystallization reagent is 2-methyl-2,4-pentanediol (MPD); MPD appears to provide both polar (hydrogen-bonding) and nonpolar packing interactions with protein molecules, thereby promoting crystallization. To determine whether other small organic molecules might be useful in protein crystallization, an array of commercially-available diols was used in crystallization attempts of hen white lysozyme, which has been crystallized in the presence of MPD as well as in a non-organic medium. In a previous Capstone project, Dan Cabrales ('04) successfully obtained crystals of lysozyme grown in the presence of MPD and in 1,6-hexanediol. The project seeks to reproduce those crystals, determine an X-ray structure from the 1,6-hexanediol-containing crystal, and obtain crystals (and structures) of lysozyme grown in the presence of other small organic molecules. Information from the studies would be used to predict novel crystallization compounds, which would subsequently be synthesized by Asst. Prof. Lin for testing as potential crystallization reagents.

Biophysical Characterization of a Bifunctional Iron-binding Protein

Researcher: Assistant Professor Virginia F. Smith

Human cytoplasmic aconitase/iron-responsive element binding protein (hIRP-1) is a 98 kDa bifunctional enzyme involved in iron regulation. The protein alternates between aconitase and mRNA binding activities depending on the intracellular levels of iron. Spectroscopic characterization, enzyme activity assays and equilibrium thermal and chemical denaturation of a recombinant form of hIRP-1 have revealed interesting properties. Specifically, hIRP-1 undergoes a multi-state unfolding transition as a function of urea, but an apparent two-state unfolding in response to thermal denaturation. As urea concentration increases, the tryptophan fluorescence intensity increases and undergoes a red shift, suggesting a quenching interaction that is relieved as the protein unfolds. A pair of tryptophans believed to be at the interface between two domains has been identified as the possible source of the observed hyperfluorescence. Enzyme activity is lost abruptly at ~2 M urea, consistent with a disruption of the active site, which is located in an interdomain cleft. The addition of a chelating agent to remove the [4Fe-4S] cluster does not significantly alter the unfolding properties of hIRP-1, suggesting that the cluster does not play a major role in the stability of the protein tertiary structure.

Investigations of Imidazolium Based Ionic Liquids in Preparation of Polymer Nanocomposites from Layer Silicates and Graphite

Researchers: Assistant Professor Paul C. Trulove; Dr. Hugh C. De Long (AFOSR); Dr. Jeffery W. Gilman (NIST), Dr. Paul Maupin (DoE) and Assistant Research Professor Douglas M. Fox (USNA)

The objectives of this research program are to evaluate, and exploit tri-alkyl-imidazolium-based ionic liquids as novel, thermally stable treatments for layered-silicates and graphite for the purpose of preparing high quality polymer nanocomposites. Initial work has demonstrated the superior thermal stability of trialkylimidazolium treated layered-silicates (montmorillonite (MMT) and fluorinated synthetic mica (FSM)). For example, the onset of thermal decomposition of the hexadecyl-functionalized dimethylimidazolium montmorillonite (DHHDIM-MMT) is over 100 ^{o}C higher that MMT treated with standard tetraalkylammonium salts. In addition, the DHHDIM-MMT has shown excellent compatibility with polyamide-6 (PA-6), and hence forms high quality PA-6/MMT nanocomposites. The DMHDIM-MMT also forms good quality mixed intercalated and exfoliated nanocomposites with polystyrene. We have also recently been the first to successfully prepare nanocomposites with polyethyleneterephthalate (PET, m.p. 290°C) using conventional extrusion and the hexadecyl-functionalized dimethylimidazolium. A variety of techniques are being used to characterize these novel layered-silicates and nanocomposits; these range from TEM, XRD, TGA/DSC, and NMR

Midshipman Research Course Projects

Function and Regulation of *Staphylococcus aureus* ClpB

Researcher: Midshipman 1/C Brian T. Barlow, USN
Adviser: Assistant Professor Tammy L. Domanski

Clp proteins comprise a family of important heat shock and stress response proteins. Until recently, there has been no information concerning the role of these proteins in the pathogen *Staphylococcus aureus*. This study pursued two aims, the regulation of expression and the function of the protein. Cultures of the bacteria were treated with a variety of stresses including temperature shifts, hydrogen peroxide treatment, and antibiotic treatment. The level of *clpB* RNA was compared with the amount of RNA from untreated samples. High and low temperatures induced *clpB* expression to varying degrees. Treatment with the antibiotic mupirocin increased the level of *clpB* RNA, and this finding has not been previously reported. Cloning of the *clpB* gene into a vector for expression in *E. coli* was the first step toward purifying and characterizing ClpB function *in vitro*.

Analysis of (±) Mefloquine & Antimalarial Investigation of West African Vegetation

Researcher: Midshipman 1/C Grant T. Bryan, USN
Adviser: Assistant Professor Clare E. Gutteridge

Mefloquine hydrochloride, a common and effective drug used to combat malaria all over the world was used prophylactically by the Marines during a deployment in Liberia. Since one third of the warfighters contracted malaria, analysis of the medications used was initiated. An attempt was made to determine the enantiomeric composition of the mefloquine in the tablets using a chiral high performance liquid chromatography. Partial separation of the two enantiomers was realized, but success will require more extensive optimization of separation parameters.

In a second investigation four plant species, used in Guinea, West Africa as natural treatments for malaria and other febrile diseases were obtained. Samples of the plants were ground up and extracted using different solvents. The resulting samples were dried and submitted for assessment of antimalarial efficacy.

Assessing the Effectiveness of the Amidine Functional Group on the Antimalarial Activity of Chalcones

Researcher: Midshipman 1/C John M. Burger, USN
Adviser: Assistant Professor Clare E. Gutteridge

Chalcones, known to posses some antimalarial activity, are readily synthesized by aldol condensation between an aldehyde and an acetophenone. The amidine is a functional group with potential to improve the antimalarial activity compounds containing it. The aim was to assess whether incorporation of an amidine would improve the antimalarial activity of chalcones. The initial target selected was 4-amidino-2',4'-dichlorochalcone. The aldehyde precursor, 4-amidinobenzaldehyde, was synthesized as its hydrochloride salt from 4-cyanobenzaldehyde in three synthetic steps. Under standard conditions its condensation with 2',4'-dichloroacetophenone was unsuccessful. Subsequent investigation of alternate reaction conditions will be required to access the target compound.

The Effect of HCH-Salicortin on Caterpillar Performance

Researcher: Midshipman 1/C Jonathan R. Dettmer, USN
Adviser: Assistant Professor Brian J. Rehill

Does HCH-salicortin possess stronger anti-herbivore activity than salicortin because of its dual hydroxy-cyclohexen-on-oyl moieties? Phenolic glycosides such as salicortin and tremulacin (found in aspen leaves) have clear linear dose effects on herbivores such as the gypsy moth caterpillar, and each compound contains a single hydroxy-cyclohexen-on-oyl (HCH) moiety. Thus, this project aimed to elucidate if phenolic glycoside effects on herbivores were due to the number of moles of HCH ingested. Initially, solid phase and liquid/liquid extraction of leaves from trees of the genus *Populus* (cottonwoods) was done to generate sufficient quantities of crude phenolic glycosides containing HCH-salicortin and salicortin. Yields of crude phenolic glycosides ranged from 3 to 5% of initial leaf dry mass. Next, these compounds were separated and purified through flash column chromatography. Based on product purity and amounts obtained, yields are ca. 1.0 and 1.5 % of initial leaf dry mass for salicortin and HCH-salicortin, respectively. Midshipman 1/C Dettmer encountered difficulties in scaling this procedure up to obtain large quantities of semi-pure and pure salicortin and HCH-salicortin, however small amounts (ca. 1.0 g) of semi-pure salicortin and HCH-salicortin were obtained. These products will be used to obtain pure substances to be used as standards for quantification by HPLC of amounts of the compounds found in leaves and artificial diets. More of both compounds must be generated to provide sufficient amounts to incorporate into caterpillar diets. Growth and performance of the caterpillars will then be tracked. This research project will continue.

Molecular Modeling Studies of Fluorinated Amino Acids

Researcher: Midshipman 1/C Jami L. Gann, USN
Adviser: Associate Professor Joseph J. Urban

An analysis of the conformational preferences of the alanine dipeptide and its β-fluoro derivative has been carried out with the MMFF molecular mechanics force field, density functional theory at the B3LYP/6-31G(d) level, and some MP2/6-31G(d,p) level calculations. Studies have been done for the molecule in both gas and aqueous phases. The preliminary results suggest that the fluorinated derivative will not exhibit conformations that are significantly different, in terms of backbone dihedrals, than the parent dipeptide. However, a different conformation is found to be the global minimum for the gas phase fluoro case (C5) than the parent ($C7_{eq}$) compound. From the Monte Carlo studies, the low energy aqueous phase conformer is α_R for both alanine and the fluoroalanine. Further studies will be directed at exploring the trifluoroalanine and branching out to different amino acids such as serine.

Analysis of *Staphylococcus aureus* Populations on Outdoor Athletic Fields

Researcher: Midshipman 1/C Rachel G. Gowins, USN
Adviser: Assistant Professor Tammy L. Domanski

Staphylococcus aureus is the number one cause of nosocomial infections in the United States. In addition, methicillin resistant *S. aureus* have been found to account for a high percentage of these infections. Recently, anecdotal evidence has suggested contraction of *S. aureus* on artificial turf fields. This project sampled three fields five times over a three month period to test for the presence of *S. aureus*. Gram staining, agglutination tests, PCR amplification and agarose gel chromatography were the main methods of identification. Although a significant amount of bacterial growth was found on the fields, only one sample (D,1,2) is potentially *S. aureus*. This sample is of particular interest because it is resistant to the antibiotic methicillin. Recently, it was found that at least two samples collected from the Naval Medical Clinic in a previous study at USNA vary from other *S. aureus mecA* sequences. *MecA* is the gene responsible for methicillin resistance, and it will be of interest to determine if the *mecA* from the environmental sample D,1,2 also carries these variations.

Isolation and Characterization of Proteins Isolated from the Psychrophile *Aquaspirillium arcticum*

Researcher: Midshipman 1/C Christina Hayes, USN
Adviser: Assistant Professor Jamie L. Schlessman

The molecular basis of cold adaptation by psychrophiles, organisms that thrive at 5-10 ^{o}C, remains enigmatic due, in part, to the relatively small number or proteins from psychrophilic organisms that have been studied. Identification and biochemical and structural characterization of additional proteins from psychrophiles would help to create a database summarizing factors related to protein stability and function at colder temperatures. Obtaining genes encoding psychrophilic proteins is nontrivial, since no psychrophilic genome has been sequenced. As a first step toward creating the psychrophilic database, *Aquaspirillium arcticum* cells were cultured and lysed. The bacterial cell lysate was filtered, then subjected to various chromatographic separation methods to identify target proteins for subsequent characterization. Gel filtration, cation-exchange, anion-exchange, and heparin-affinity columns were utilized. Significant protein binding occurred using the cation-exchange and heparin-affinity columns, and appreciable purification was achieved using the heparin-affinity column. These results are consistent, since heparin-affinity columns have been used successfully to purify nucleic acid-binding proteins. Such proteins would be expected to contain a positively-charged region that also binds to cation-exchange columns. This positively-charged region of the protein presumably binds to the negatively-charged phosphate groups of the nucleic acid substrate. Additional work is required to purify the proteins to homogeneity so that partial amino acid sequencing may be performed and oligodeoxyribonucleotides may be designed specific to the target genes. Subsequent amplification of the genes would allow for large-scale recombinant production of the target proteins to facilitate protein characterization.

Analysis of Soil at Antietam National Battlefield

Researcher: Midshipman 1/C Luke E. Kelvington, USN
Adviser: Associate Professor Daniel W. O'Sullivan

Blood shed on a battlefield contains metals such as Zn, Cu, Fe, and Mg. The hypothesis of this project was that the concentration of these metals in the soil could be used to identify where a greater concentration of troops were killed. The Antietam National Battlefield was used as the testing grounds for this hypothesis. The procedure for how the samples were digested and then analyzed was developed over the course of the 1st semester and put to use on the actual battlefield samples during the spring semester. The results were overall inconclusive and much more analysis would need to be completed in order to determine if the soil actually could be used to determine if more blood was shed in certain areas. The actual amounts of the elements found in the soil were within the range of normal soil samples. This led us to believe with more analysis more conclusive results could be obtained.

Nucleoside Analogues as Potential Antiviral Agents

Researcher: Midshipman 1/C Michael J. Miller, USN
Adviser: Assistant Professor Debra K. Dillner

Viral diseases are the leading cause of death from infectious diseases world-wide. The most effective means of battlingviral diseases has been vaccination. For those diseases, such as viral enteritis, for which vaccination has not been as effective, few drug treatments are available. For this reason, new classes of compounds which might exhibit anti-viral activity are of great interest in medicine and the military. One such class of compounds are nucleoside analogues which are diphosphonates. Some nucleoside analogues in other classes have shown significant anti-viral activity, mainly as viriostatic agents. These compounds primarily act against viruses by interfering with viral replication. A new class of compounds, with the sugar moiety of the naturally occurring nucleosides is being investigated. In these derivatives, the sugar is replaced by an alkyl chain, each end of which is terminated by a phosphonate group. The phosphonate group has a stable carbon-phosphorus bond which should resist biochemical degradation, while also being recognized by various biosynthetic pathways as DNA precursors. In the past year, preparation of the phosphonate capped alkyl chains has been initiated. Significant process in understanding and completing these syntheses has been gained. Based on the contributions of this project, additional synthetic studies, including coupling the alkyl chains to nucleotide bases will be undertaken next year.

Effect of Functional Group Type on Sol-Gel Capillary Electrochromatography

Researcher: Midshipman 1/C Nicholas A. Roa, USN
Adviser: Associate Professor Christine L. Copper

Capillary electrochromatography (CEC) is a hybrid method of liquid phase separation. It combines mechanisms from capillary electrophoresis (CE) and high performance liquid chromatography (HPLC). Sol-gels can be used as stationary phases in CEC. A sol-gel is a silica based composition which is spongy and porous in nature. Every sol-gel process requires four basic reactants and involves two basic reactions. The reactants are a metal alkoxide precursor, suitable solvent system, catalyst and water. To make a sol-gel function as a suitable stationary phase in CEC, a structural foundation is needed to serve as support for the network of condensed precursors. The porogen provides that foundation. Once all of these reactants have been combined, the sol-gel process requires a base strong enough to drive the condensation reaction.

Previously, hydrophobic functionality was incorporated into sol-gels <u>after</u> initial gel formation. In this light, current efforts have focused on reducing the time needed to prepare a gel by utilizing alkylated sol-gel precursors <u>during</u> the gel formation step. This produces a gel with the desired hydrophobic character in a single step, significantly reducing the time necessary to achieve a functionalized gel. Using a base gel formulation with methyl functionality, we planned to explore the effects of doping the sol-gel with precursors containing ethyl functionality on the separation of nitroaromatic explosive residues. To date, numerous sol-gel formations have been optimized and CEC columns reproducibly created. However, the goal of using these columns to separate explosives residues has yet to be fulfilled.

The Effect of Developmental Trajectory on Sycamore and Sweetgum Tannin Content

Researcher: Midshipman 1/C David J. Rusthoven, USN
Adviser: Assistant Professor Brian J. Rehill

Condensed tannins often comprise a sizeable proportion of a plant's dry mass, thus they are a good initial target for the investigation of the role of developmental trajectory on plant secondary/ defensive chemistry. Foliage was collected from the high (mature) and low (juvenile) zones of the canopies of eight mature trees as well as from twelve saplings of both species. For each sample, particular leaves were collected from each shoot (2nd and 3rd leaves for sycamore, 4th and 5th for sweetgum) and labeled 'sample', all other leaves of each sample were considered 'bulk'. Measurements of mean soluble condensed tannin concentration for the 'bulk' collections were significantly higher than those for the 'sample' collection ($p = 0.036$), thus our method of leaf sampling appears to be required to produce uniform results. For the eight mature trees, using both 'bulk' and 'sample' as replicates from each tree,

condensed tannin concentrations were greater in the high (mature) zone of the canopy (p = 0.001). However, when only the 'sample' leaves were considered, condensed tannin concentrations of saplings were greater than both the high (p = 0.043) and low (p =0.001) zones of the canopy, but concentrations did not differ between high and low zones (p = 0.167), likely due to high variance and a low sample size. Nevertheless, these results indicate the presence of adevelopmental trajectory in both trees. The project will continue in AY06.

Substrate Binding Properties of Methionine Sulfoxide Reductase

Researcher: Midshipman 1/C Brian C. Schexnayder, USN
Adviser: Assistant Professor Virginia F. Smith

Aerobic metabolism makes life possible for large land-based plants and animals, but it also generates highly reactive intermediates and by-products in the form of hydroxyl radicals, superoxide anions and hydrogen peroxide. Within the cell, these reactive oxygen species attack biological macromolecules such as proteins, DNA and lipids, producing covalent modifications that can affect both function and structure. One amino acid residue in proteins that is particularly sensitive to oxidation is the sulfur-containing side chain of methionine. Methionine oxidation, in the form of sulfoxide groups, has been implicated in numerous and iverse biological phenomena including pathology of human diseases, the process of aging and metabolic regulation. Fortunately, methionine oxidation, unlike most other oxidative covalent modifications, can be reversed enzymatically by the enzyme methionine sulfoxide reductase (MsrA). Although the enzyme mechanism for methionine sulfoxide reduction has been extensively characterized, the mechanism by which MsrA recognizes damaged proteins has not. Since MsrA can repair oxidized methionine side chains in a variety of contexts we propose that the enzyme recognizes its substrate using generic features shared by many denatured proteins. We will describe preliminary efforts to test this hypothesis using the enzyme staphylococca nuclease as a model substrate for repair. Specifically, we have developed an *in vitro* system to measure MsrA repair activity of oxidized methionines directly by MALDI-TOF mass spectrometry and indirectly by quantitation of enzyme activity.

Determination of Response of a Chemiluminescent System to Accurately Measure Concentrations of Hydrogen Peroxide in the Atmosphere

Researcher: Midshipman 1/C Michael J. Siedsma, USN
Adviser: Associate Professor Daniel W. O'Sullivan
Sponsors: National Science Foundation (NSF) Physical Meteorology Program
and Office of Naval Research (ONR)

This experiment compared two techniques for determining the concentration of hydrogen peroxide. The method of high performance liquid chromatography (HPLC) using a fluorescence detector was compared to a chemiluminescent system with a photo multiplier tube detector. The systems were compared on reliability, reproducibility, and efficiency in analyzing multiple consecutive samples. It was determined that the chemiluminescent system is a faster more efficient method for measuring hydrogen peroxide. Also, the concentrations of the stock solutions of this project were determined using titration, complexation, and spectrophotometric methods. The chemiluminescent system was taken to Antigua for field tests during the months of December and January 2004-2005, and after two months of data collection was flown back to our laboratory at the Naval Academy. A pH optimization of the carbonate buffer was then performed as well as studies on replacing the carbonate buffer with a borate buffer. Finally, a synthesized acridinium ester (synthesized by Midshipman 1/C Ryan Tuttle) was tested alongside the original ester used. It showed evidence of having a much higher purity.

Investigation of Substituent Effects on ^{13}C NMR Carbonyl Chemical Shifts

Researcher: Midshipman 1/C John T. Stanley, USN
Advisers: Assistant Professor Debra K. Dillner and Assistant Professor Shirley Lin

In this project, the carbon-13 chemical shifts of various monosubstituted acetophenones were obtained, primarily from literature sources. The effect of substituents on the aromatic ring upon the chemical shift of the carbonyl carbon was investigated and several definite trends were seen. Each of the substituents had an effect consistent with its inductive and resonance properties. These effects were summarized as additivity values called Substituent Chemical Shifts (SCS) values. The ability of these SCS values to predict the carbonyl resonance of multiply substituted acetophenones was tested. The data shows that for the most part, carbonyl carbon NMR shifts are additive when multiple substituents are present. The inductive and resonance effects of the substituents are incorporated in the SCS values and if these are the only factors present, the chemical shift can be predicted within 0.5 ppm. Induction and resonance had opposing effects on the carbonyl chemical shift. Linear free energy studies showed induction is more important than resonance in determining carbonyl chemical shifts. The one type of substituent which was anomalous in its effect was a hydroxyl group. The anomalous results could be due to hydrogen bonding between the hydroxyl group and the carbonyl, either inter- or intramolecularly. A NMR study was undertaken to explore this factor for 3- and 4-hydroxyacetophenone, which should exhibit intermolecular hydrogen bonding. The results of this study show an approximately 5 ppm contribution to chemical shift of the carbonyl from the hydrogen bonding. Preliminary studies of intramolecular hydrogen bonding have begun and the results of this project will be submitted for publication.

Prediction of ^{13}C NMR Chemical Shifts of Carbonyl-Containing Compounds

Researcher: Midshipman 1/C John T. Stanley, USN
Advisers: Assistant Professor Shirley Lin, Assistant Professor Debra K. Dillner,
and Dr. Daniel Traficante, Naval Academy Preparatory School (NAPS)

The ability to predict ^{13}C NMR shifts of organic compounds is useful in the determination of chemical structure. The prediction of the ^{13}C chemical shifts of carbonyls, a common functional group, has not been as fully developed as the methods chemical shift prediction for other functional groups such as alkanes, alkenes, and benzenes. A searchable database of benzaldehyde and acetophenone carbonyl chemical shifts has been created and from this a table of substituent increments for various electron-donating and electron-withdrawing substituents has been developed. We demonstrate that the ^{13}C NMR shift of the carbonyl can be predicted for many di- and tri-substituted benzaldehydes and acetophenones through simple additivity of the substituent increments. The magnitude and sign of the increments for various substituents have been explored using linear free energy relationships and correlated to the Mulliken charge of the carbonyl carbon using a molecular modeling program (PC Spartan^{TM}). Deviations from additivity on the order of 4-6 ppm are observed when substituents capable of hydrogen bonding are present as demonstrated by NMR dilution experiments.

Synthesis of Sulfonated Polymers in Mesoporous Silica as Potential Electrochemical Separator Materials

Researcher: Midshipman 2/C Jon D. Stockton, USN
Adviser: Associate Professor Joseph F. Lomax

Ordered mesoporous silica with enlarged pore sizes (2-15 nm) can now be made reliably in large amounts through a nonionic assembly pathway under acidic conditions. Uniform polymer coatings can be made inside these materials by radical polymerization. In this same article, they took the Organic – Inorganic composite nanoporous material and reacted with sulfuric acid to make a sulfonated compound. This project investigated making this same material, and characterizing its ion conducting and physical properties. Attempts have been made to synthesize a robust ion conductor that may have promise in electrochemical applications.

Optimization of Gel Porosity in Sol-Gel Capillary Electrochromatography

Midshipman 1/C Erika M. Teichert, USN
Adviser: Associate Professor Christine L. Copper

Capillary electrochromatography (CEC) is a hybrid method of liquid phase separation. It combines mechanisms from capillary electrophoresis (CE) and high performance liquid chromatography (HPLC). Previously, sol-gels have been used as stationary phases in capillary electrochromatography (CEC) for the separation of solutes including inorganic anions and polycyclic hydrocarbons. It has been shown that the porosity of a CEC sol-gel column has a vast influence on the separation performance of the column. Porosity determines several important factors including backpressure, peak capacity, and separation efficiency. Water content during the sol synthesis is the most significant parameter when determining porosity. In this work, novel sol-gels containing methyl functional groups were formed in a one-step process inside of the capillary. The effects of reactants, reaction conditions, and rinsing procedures on the separation of nitroaromatic explosives residues using sol-gel CEC were studied. Thus far, successful separation of seven explosive residues has been optimized by altering conditions such as mobile phase composition, injection time, and separation voltage.

Molecular Modeling Studies of Fluoroolefin Peptide Mimetics

Researcher: Midshipman 1/C Brendon G. Tillman, USN
Adviser: Associate Professor Joseph J. Urban

This research involved a computational investigation of model fluorinated peptide mimetics. The compounds focused on in this work incorporated the fluoroolefin group as a replacement for the peptide bond. A series of model compounds was chosen that included dipeptide mimics that act as inhibitors of the dipeptidyl peptidase IV enzyme and pentapepdide mimics of the enkephalin neuropeptides. The results of this ongoing study indicate that the peptide mimics have characteristics that are similar to peptides with respect to geometry and charge distribution. The mimetics were found to engage in hydrogen bonding interactions that are similar in configuration to those of the peptides, but much weaker in magnitude. The preliminary results indicate that these differences in hydrogen bonding will manifest themselves in differences in conformational preferences between the mimetics and the peptides as larger systems are investigated.

The Effect of Developmental Trajectory pn Tulip Poplar Tannin Content

Researcher: Midshipman 1/C John A. Vigilante IV, USN
Adviser: Assistant Professor Brian J. Rehill

Samples were taken from the high (mature) and low (juvenile) zones of the canopy of eight mature tulip poplar trees. Unlike the project described above, both soluble and bound (cell-wall connected) condensed tannin concentrations were measured. Soluble condensed tannin concentrations did not differ between the two zones ($p = 0.967$), as did bound condensed tannin concentrations ($p = 0.421$). Thus this study produced no evidence for a developmental trajectory of condensed tannin concentrations in tulip poplar, and as such, this species will serve as an excellent contrast to sycamore and sweetgum. Furthermore, sample and bulk concentrations for both parameters did not differ, thus at least for condensed tannins, collection method does not alter results. This may indicate greater within-shoot homogeneity in phytochemistry for tulip polar than sycamore and sweetgum, also making this species an excellent contrast. I will continue investigation into the phytochemistry of this species, as well as investigating the role of condensed tannins and other chemical parameters in leaf decomposition

Differential Scanning Calorimetry and Thermogravimetric Analysis of Cerium Nitrate Treated Towels.

Researcher: Midshipman 1/C Cicely A. Waters, USN
Adviser: Associate Professor JudithAnn R. Hartman

Solutions of Cerium (IV) Nitrate in Nitric Acid are used to clean surfaces contaminated with radioactive dust during the decommissioning of weapons production facilities. A recent fire during decommissioning work led to a study of the effect of Cerium Nitrate on the self-heating properties of cotton towels. This work used classic oven experiments with piles of treated towels. At least three different sample sizes were tested to characterize the self-heating behavior of the material using this oven method. At each sample size, three to six tests with durations of days or weeks were done to adequately determine the critical temperature for self-heating for that sample size. We have extended this work using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) to measure kinetic constants for the self heating reactions of cotton towels in the presence and absence of acidic Cerium Nitrate cleaning solution. The results have been analyzed to validate the use of TGA or DSC as a replacement for the more time intensive ignition studies and to provide more detailed kinetic data regarding the effect of the Cerium Nitrate on heating properties of cotton towels than are available through the use of the classical oven test methods.

Midshipmen Capstone Projects

Molecular Dynamics Analysis of the Detonation of Cubane

Researcher: Midshipman 1/C David J. Blossom II, USN
Adviser: Professor Mark L. Elert

Cubane is a relatively new synthetic chemical which has great promise for use in explosives and propellants. Very little experimental data is available for the detonation properties of interest for this material. Using molecular dynamics simulations employing a reactive empirical bond order potential, the detonation threshold, detonation velocity, and temperature and pressure profiles of the shock wave in detonating cubane were determined.

Development of an Atomic Absorption Experiment for Use in the Integrated Laboratory Curriculum

Researcher: Midshipman 1/C Louie A. Ferro, USN
Adviser: Associate Professor Maria J. Schroeder

Excess iron accumulation in the human body is a very prominent topic in today's scientific community due to its known harmful effects. Because of this, determining iron concentrations in food and drink samples is an aspect that is often studied in the laboratory. Atomic absorption (AA) spectroscopy provides an excellent method for determining the concentration of metals in various sample matrices. In this project, a new laboratory experiment was developed to teach undergraduate students the theory behind atomic absorption spectroscopy, allow them to utilize Flame-AA instrumentation in the analysis, and spark student interest in a health-related topic. In the developed experiment, students are given the choice of testing a variety of different food samples for iron. Furthermore, they are allowed to select their method of analysis, either utilizing a calibration curve or a standard addition method. Giving students the chance to make decisions in the laboratory allows them to become more independent and interested in the outcome of their experiment. Coupled with a web-based tutorial on AA, the probability for student learning is enhanced.

Synthesis of Potential Electrochemical Separators for Use in Direct Methanol Fuel Cells by Separation of Pillaring and Acidic Functions

Researcher: Midshipman 1/C James D. Ford, USN
Adviser: Associate Professor Joseph F. Lomax

The goal of this project is to find ion exchange membranes which are thermally table at temperatures above 150°C. This goal represents a fuel cell membrane able to operate at expected temperatures for multiple purposes, which will not degrade during function. Two complementary lines of layered zirconium phosphonate /phosphate research converge in this project 1) the thermal stability and conductivity of zirconium phosphonates substituted with acidic functional groups, and 2) the ability to create pillared α-$Zr(O_3P\text{-}R\text{-}P\ O_3)$ compounds, varying the pillar length by varying the R radical. The pillaring holds the Zr-phosphate-like layers together thus preventing the swelling and contracting which prevented previous acid-substituted phophonates from making an effective electrochemical separator. By separating the functions of ion conductivity and pillaring, the synthesis of the compound is simplified while maintaining thermal and mechanical stability (from the pillar) and high ion conductivity (from the substituted phosphonate). This approach has been successful in making other mixed phosphonate/diphosphonate zirconium layered compounds. The important part is to match the size of the diphosphonate and the substituted phosphate and to choose the proper functional group on the phosphonate. The two-part thrust of the research deals with first -- the synthesis of different phosphonate and diphosphonate compounds and second – taking the resulting phosphonate and diphosphonate and reacting them with a Zr^{4+} salt. The synthesis of the diphosphonates has been a larger challenge than anticipated. Two terminal diphosphonates, the 1, 10-diphonphonodecane and the 1, 12-diphosphonododecane, have been synthesized.

Atomic Absorption Spectroscopy – An Interactive Approach to Learning

Researcher: Midshipman 1/C Audrey J. Peterman, USN
Adviser: Associate Professor Maria J. Schroeder

Students at the Naval Academy have complete access to the Internet, making it an ideal resource for instruction. Because the Internet can utilize stimulating visuals, animation, and interaction where paper handouts cannot, the Internet is especially useful to chemical educators who seek ways to present sometimes difficult concepts and stimulate student interest. The goal of this project was to create an online, accessible tutorial for use in the Integrated Laboratory (IL) courses, in support of an experiment on atomic absorption (AA) spectroscopy. The tutorial was designed to enhance student understanding of atomic absorption spectroscopy concepts, to explain the operation of the atomic absorption instrument, and to help in analyzing the results of atomic absorption experiments. While the tutorial was intended for use by chemistry students as a pre-lab exercise, it could also be utilized for training research students and faculty interested in using the instrument. A rough draft of the tutorial was tested by a group of IL students to obtain a preliminary assessment of this learning tool. Although the sample size was small, preliminary results of the assessment indicate the usefulness of the tutorial in student learning.

The Detonation Chemistry of Cubane

Researcher: Midshipman 1/C Antonia K. Shey, USN
Adviser: Professor Mark L. Elert

Cubane is a novel explosive material in which energy is stored in the form of strained carbon-carbon bonds. Very little is know of the mechanism of energy release in the detonation of this material. Using adaptive intermolecular reactive empirical bond order (AIREBO) potentials, a molecular dynamics study of the chemical reactions of cubane at a shock front was undertaken. The shockwave propagation and the products formed were simulated using time steps that are a fraction of a femtosecond. Population profiles of various product species versus time from the impact of collision were produced in order to better understand the reactions occurring.

Synthesis of 10-Methyl-9-(*p*-Formylphenyl)-Acridinium Carboxylate Trifluormethansulfonate for Atomospheric H_2O_2 Detection

Researcher: Midshipman 1/C Ryan J. Tuttle, USN
Advisers: Associate Professor Craig M. Whitaker and Associate Professor Daniel L. O'Sullivan

The acridinium ester, 10-methyl-9-(*p*-formylphenyl)-acridinium carboxylate trifluoromethanesulfonate, was synthesized via a three-step synthetic procedure for use in determination of H_2O_2 concentration in atmospheric samples through a chemiluminescence technique. The structure of the final synthesized compound was verified through the use of ^{1}H NMR spectroscopy. The purity of the synthesized sample was confirmed by comparing chemiluminescent outputs of a previously obtained acridinium ester and the synthesized ester when mixed with a water sample containing H_2O_2. The synthesized ester produced far greater chemiluminescence outputs than the purchased ester and was more useful in the determination of the concentration of H_2O_2 in atmospheric samples.

Professional Publications

Journal (Refereed) Manuscripts

CHATEAUNEUF, G. M., Assistant Research Professor, MIKULSKI, Paul T., Assistant Professor (USNA Physics Department), GAO, G., Assistant Research Professor, and HARRISON, Judith A**.,** Professor, "Compression- and Shear-Induced Polymerization in Model Diacetylene-containing Monolayers", *J. Phys. Chem. B*, Vol. 108, pp. 16626-16635, 2004.

Molecular dynamics simulations were used to examine the response of monolayers composed of alkyne chains, which contain diacetylene moieties, to compression and shear. The simulations showed that both compression and shear result in cross-linking, or polymerization, between chains. Irregular polymerization patterns appeared among the carbon backbones, as opposed to the long rows of π-bonded chains, as is the case when UV radiation is used to initiate polymerization. The vertical positioning of the diacetylene moieties within the alkyne chains (spacer length) and the sliding direction influenced the pattern of cross-linking and friction. In addition, chemical reactions between the chains of the monolayer and the amorphous carbon tip occurred when diacetylene moieties were located at the ends of the chains closest to the tip. These adhesive interactions increased the friction.

CHEEK, Graham T. Professor, (co-author), "Impedance Studies of the Passive Film on Aluminum," *Corrosion Science*, accepted for publication.

Impedance spectroscopy has been used to study the characteristics of aluminum in 0.10 M NaCl solution at potentials below the pitting potential (-1.50 VSCE to -0.70 VSCE). Two semicircular impedance features have been identified over this range of potentials, the first of which broadens considerably as potential increases. The resistance derived from the high-frequency feature is observed to increase monotonically as the potential is increased up to the point where metastable pitting begins to occur. Previous work using XPS and x-ray absorption near edge structure (XANES) data allowed a calculation of the concentration of chloride in the passive film, and a correlation has been established between the impedance of the first semicircular feature and the concentration of chloride in the passive film. The relationship suggests that incorporation of chloride into the passive film results in a more resistive film. At the onset of metastable pitting, both the impedance and chloride concentration decrease from the measured maxima. In contrast to XPS studies, the impedance results do not reveal oxide thinning prior to the onset of metastable pitting. Modeling from impedance data indicates that the thickness of the oxide layer sampled by impedance is much thinner than the oxide measured with surface analytical techniques, suggesting that the impedance method senses only the space charge layer in the oxide and not the total film thickness.

ELERT, Mark L., Professor, (co-author), "Nanoscale View of Shock-wave Splitting in Diamond", *Metallurgical and Materials Transactions A*, Vol. 35, pp. 2647-2650, 2004.

Molecular dynamics simulations of shock wave propagation in the <110> crystallographic direction of diamond were carried out using an empirical reactive bond order (REBO) potential. A split two-wave shock structure due to a lattice transformation is observed above a piston velocity threshold of $u_p \approx 1.8$ km/s corresponding to the Hugoniot elastic limit of 125 ± 15 GPa. This transition is triggered while the temperature increase in the leading shock remains negligibly small in comparison to the melting temperature of diamond and is limited to moderate shock strengths.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-authors), "Dissolution and Regeneration of *Bombyx Mori* Silk Fibroin using Ionic Liquids," *Journal of the American Chemical Society,* Vol. 126, No. 44, pp. 14350-14351, 2004.

Natural silk fibers have outstanding mechanical properties that rival the most advanced synthetic polymers. Compared to the limited number of molecular solvents available today, ionic liquids have taken the spotlight as green, designer solvents, with many combinations that offer an unprecedented versatility and tunability. In this work, we test the suitability of ionic liquids for dissolving and regenerating silkworm (*Bombyx mori*) silk and examine the structural properties of silk films cast from ionic liquid solutions.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-authors), "Preparation of Homogeneously Dispersed Trialkylimidazolium Compatibilized Multi-Walled Carbon Nanotube / Polystyrene Nanocomposites via Melt Extrusion," *Advanced Functional Materials,* Vol. 15, pp. 910 – 916, 2005.

Trialkylimidazolium-tetrafluoroborate, (IM) compatibilized, multiwalled carbon nanotubes (MWNT) are used to prepare well dispersed polystyrene (PS) IM-MWNT nanocomposites via melt extrusion. FTIR of the 1:1 imidazolium treated MWNTs provides direct evidence for a π-cation, nanotube-imidazolium interaction. Quantitative TEM image analyses reveal superior dispersion of the MWNTs in the presence of the imidazolium. DSC reveals no phase separated imidazolium and TGA shows an increased thermal stability in the PS/ (1:1) IM-MWNT nanocomposite.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-authors), "TGA Decomposition Kinetics of 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate and the Thermal Effects of Contaminants," *J. Chem. Thermodynamics*, in press.

Thermal gravimetric analysis (TGA) has been used to determine the kinetics of decomposition for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIM][BF_4]) and to identify the effects of contaminants on the decomposition temperatures. Data was collected from both isothermal and constant ramp rate programs for the decomposition of [BMMIM][BF_4] under N_2. The isothermal data was fit to a global kinetic model and the apparent Arrhenius parameters were determined. The constant heating rate data was used to determine the apparent activation energy using the isoconversional method developed by Friedman. The effects of up to 10 wt% water, NH_4BF_4, NH_4Cl, and [BMMIM][Cl] impurities on [BMMIM][BF_4] decomposition temperatures were investigated. The only contaminant to significantly affect the decomposition was NH_4Cl, resulting in some decomposition at the temperatures associated with [BMMIM][Cl] decomposition.

GREENE, Philip A., Midshipman 1/C (USN) and COPPER, Christine L., Associate Professor, (co-authors), "Colorimetric Detection of Uranium(VI) on Building Surfaces After Enrichment by Solid Phase Extraction," *Talanta*, Vol. 66, No. 4, pp. 960-965, 2005.

A method for detecting and quantifying uranium (VI) levels on building materials that include concrete, Plexiglas, glass and steel surfaces is presented. Uranium (VI) was extracted from building material surfaces using a pH 2.2 buffer rinse and, subsequently complexed by an organic chelating agent, arsenazo III. The application of a uranium-chelating molecule, arsenazo III, allows for concentration enhancement using C_{18} solid phase extraction and colorimetric detection of the uranium complex using ultraviolet–visible spectroscopy at 654 nm. The method has a detection limit (based on 3σ) of 40 ng/L (5 ng/cm^2) and an overall extraction efficiency greater than 80% for each surface type (concrete, Plexiglas, glass, steel). Methods to prevent interference by metal ions commonly found on building materials are discussed.

GREENE, Philip A., Midshipman 1/C (USN), and COPPER, Christine L., Associate Professor, (co-authors), "Recovery and Detection of Uranium (VI) From Building Materials", Department of Energy Scientific and Technical Information Bridge (http://emsp.em.doe.gov/workshop_pdfs/california_2004/p038.pdf), #825905, 2004.

As a legacy of the United States' 50 year old nuclear weapons program, the Department of Energy is responsible for cleaning up and decommissioning contaminated sites that were used for the production of these weapons. The method presented here addresses the problem of detecting and quantifying uranium (VI) in concrete. Specifically, the uranium (VI) is removed from concrete surfaces using a low pH buffer rinse that dissolves the surface layer. The amount of uranium in the wash solution can be quite low, even with extraction efficiencies exceeding 50 %. Therefore, the uranium is complexed with an organic chelating agent (arsenazo III) and concentrated using C18 solid phase extraction. Because the absorbance maximum of arsenazo III shifts upon binding to uranium, the concentrated complex can be detected using ultraviolet-visible spectroscopy. Low part-per-billion levels of uranium (VI) in cement can be detected by this method. Results of work related to other building material s such as stainless steel and plexiglass will also be reported.

HARTMAN, J.R., Associate Professor, "Ignition Studies of Cerium Nitrate Treated Towels", *Fire and Materials*, accepted for publication.

This study evaluated the ignitability of cotton towel material saturated with an oxidizer solution of 0.5 N cerium(IV) nitrate in 2 N nitric acid. Four types of ignition testing were performed in this work; self-heating oven tests, hot object ignition tests, radiative smoldering ignition tests, and piloted flaming ignition/burning rate tests. Results indicate that cerium nitrate significantly enhances the ignitability of the towels. Self-heating properties of cerium nitrate treated towels were measured using the standard constant temperature oven method described by Bowes. Based upon these self-heating properties, self-heating is not a hazard for storage scenarios other than bulk storage (depths of several meters) of cerium nitrate treated towels at room temperature. Surface ignition for hot objects was observed for object temperatures as low as 250ºC placed upon room temperature cerium nitrate treated towels. Ignition for hot objects buried within a pile of towels occurred for object temperatures as low as 230ºC. Radiant heating tests of cerium nitrate treated towels showed initiation of smolder at heat fluxes as low as 3 kW/m^2 at surface temperatures as low as 175ºC. This compares with ordinary cellulosic materials that require 7-8 kW/m^2 heat fluxes and temperatures of 250ºC. All four scenarios demonstrate enhanced ignitability and burning rates of cerium nitrate treated towel.

MIKULSKI, Paul T., Assistant Professor (USNA Physics Department), GAO G, Assistant Research Professor, CHATEAUNEUF, G. M., Assistant Research Professor, and HARRISON, Judith A., Professor, "Contact Forces at the Sliding Interface: Mixed vs Pure Model Alkane Monolayers", *Journal of Chem. Phys*., Vol. 122, pp. 024701-1-024701-9, 2005.

> Classical molecular dynamics simulations of an amorphous carbon tip sliding against monolayers of n-alkane chains are presented. The tribological behavior of tightly packed, pure monolayers composed of chains containing 14 carbon atoms is compared to mixed monolayers that randomly combine equal amounts of 12 and 16 carbon-atom chains. When sliding in the direction of chain cant under repulsive (positive) loads, pure monolayers consistently show lower friction than mixed monolayers. The distribution of contact forces between individual monolayer chain groups and the tip shows pure and mixed monolayers resist tip motion similarly. In contrast, the contact forces ``pushing" the tip along differ in the two monolayers. The pure monolayers exhibit a high level of symmetry between resisting and pushing forces which results in a lower net friction. Both systems exhibit a marked friction anisotropy. The contact force distribution changes dramatically as a result of the change in sliding direction, resulting in an increase in friction. Upon continued sliding in the direction perpendicular to chain cant, both types of monolayers are often capable of transitioning to a state where the chains are primarily oriented with the cant along the sliding direction. A large change in the distribution of contact forces and a reduction in friction accompany this transition.

MIKULSKI, Paul T., Assistant Professor (USNA Physics Department), and HARRISON, Judith A., Professor, (co-authors), "Effect of Filling on the Compressibility of Carbon Nanotubes: Predictions from Molecular Dynamics Simulations", *Journal of Nanoscience and Nanotechnology*, Vol. 5, pp. 536-541, 2005.

> The compressibility of filled and empty (10,10) carbon nanotubes (CNTs) was examined using classical molecular dynamics simulations. Filled nanotubes contained C_{60}, CH_4, Ne, n-C_4H_{10} molecules and n-C_4H_7 molecules that were covalently cross-linked to the inner CNT walls. In addition, nanotubes filled with either a hydrogen-terminated carbon nanowire or a carbon nanotube of comparable diameters were also considered. The forces on the atoms were calculated using a many-body reactive empirical bond-order potential and the adaptive intermolecular reactive empirical bond-order potential for hydrocarbons. The butane filled system showed a unique yielding behavior prior to buckling that had not been observed previously. Cross-linking the molecules to the inner CNT walls did not affect the stiffness of the filled nanotube systems and removed the yielding response. The mechanical response of the nanowire filled CNT was remarkably similar to the response of the similarly sized multi-walled CNT.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Long-term Variations in the Levels of Hydrogen Peroxide, Methylhydroperoxide and Selected Compounds over the Pacific Ocean", *Journal of Geophysical Research - Atmospheres*, Vol. 109, (D15), Art. # D15S13, 2004.

> The National Aeronautics and Space Administration's Global Tropospheric Experiment (NASA-GTE) program has conducted five sampling programs examining the Pacific troposphere from 1991 to 2001. Flights on two aircraft, a P3-B and DC-8, sampled the Pacific troposphere at altitudes from 0.5 km to 13 km and from 130 °E to 115 °W and from 65°N to 70°S. Long-term trends in the observed species mixing ratios in different geographic regions are presented. Changes in species mixing ratios are discussed with respect to changes in source, transport, and photochemical production and loss processes over the decade study period. CH_4 and CO_2 exhibited average annual mixing ratio increases of 6.39 ppbv yr^{-1} and 1.92 ppmv yr^{-1}, respectively. O_3, CO, and NO all exhibit significantly higher mixing ratios in the north Pacific troposphere in the spring than in the fall. However, there is no clear annual trend for these species. H_2O_2 mixing ratios were 38 ± 16% higher [Δ(fall-spring) 258 ± 34 pptv], and CH_3OOH was 61 ± 15% higher [Δ343 ± 76 pptv] through out the Pacific troposphere in the fall than in the spring. During 2001 SO_2 loading in the north Pacific is 2-3 times larger than during earlier years. Anthropogenic tracer gases, C_2H_6, C_3H_8, C_2H_2, and C_2Cl_4, do not exhibit comparable increases in their average mixing ratios during the decade study period. CH_3I, a tracer for oceanic emission also does not exhibit an increase in 2001. Sulfur

loading characterized by SO_2 also does not exhibit a clear annual trend. The enhanced sulfur loading during 2001 appears to have resulted in a suppression of H_2O_2 mixing ratios in the lower troposphere throughout the mid-latitude north Pacific.

REHILL, Brian J., Assistant Professor, (co-author), "All Effects of a Gene on the World: Extended Phenotypes, Feedbacks, and Multi-level Selection", *Ecoscience*, Vol. 12 (1), pp. 5-7, 2005.

This publication was a rebuttal to JM Biernaskie and JG Timerman's 'The overextended phenotype' (Ecoscience 12(1): 3-4), in which they took exception to our use of Richard Dawkin's term 'extended phenotype'. While some ecologists and evolutionary biologists adhere to a rather narrow and potentially restrictive definition, we use Dawkin's own sensu lato definition of 'all the effects of a gene on the world'. In contrast to Biernaskie and Timerman's assertion, this broad sense allows scientists to get at far reaching consequences of genes, such as the plant condensed tannin genes which were discussed in several of our publications cited by Biernaskie and Timerman. Thus, a genetically controlled trait such as condensed tannin concentration of Populus leaves has consequences not only for the tree, but the community of animals that live in and around the tree as well as the ecosystem of which the tree (and its genes) are part. A narrow interpretation of extended phenotype would thus totally miss the importance of genes of dominant organisms such as Populus.

REHILL, Brian J., Assistant Professor, (co-author), "Foliar Phenolic Glycosides from *Populus fremontii*, *Populus angustifolia,* and Their Hybrids", *Biochemical Systematics and Ecology,* Vol. 33 (2), pp. 125-131, 2005.

Phenolic glycosides that contain an HCH (hydroxyclo-hexen-on-oyl) moiety, such as salicortin and tremulacin, possess known, dose-dependent anti-herbivore effects. As part of a large collaborative project on the ecology, evolution, and genetics of a hybrid Populus system, we determined the presence of such compounds in the leaves of both wild and cultivated trees. Salicortin (1) and HCH-salicortin (2) were isolated and identified from the foliage of Populus fremontii and its F-1 hybrids with Populus angustifolia. Salicortin, but not HCH-salicortin, also occurred in P. angustifolia and complex backcrosses to angustifolia. Concentrations ranged from 0 to 17.5% dry weight for salicortin and 0 to 5.9% dry weight for HCH-salicortin. HCH-salicortin may possess potent anti-herbivore activity as it contains two of the hydroxycyclo-hexen-on-oyl moieties known to confer such activity to salicortin. Further, this compound may be a useful chemotaxonomic character within the genus Populus, since it appears to occur in section Aigeiros but not in section Tacamahaca.

SCHLESSMAN, Jamie L., Assistant Professor, (co-author), "Stabilization of Internal Charges in a Protein: Water Penetration or Conformational Change?" *Biophysical Journal*, Vol. 87, pp. 3982-2894, 2004.

Protein structure dogma has long indicated that the ionizable amino acid side chains of proteins should be located at the protein surface, although in some proteins an ionizable group may be embedded in an apolar internal region. Protein destabilization may result from such buried ionizable groups, with concomitant triggering of conformational changes in response to pH variations. Because of the prohibitive energetic cost of transferring a charged group from water to an apolar medium, other stabilizing factors must be involved, such as ionization-induced water penetration or structural changes. To examine the role of water penetration, ^{17}O and ^{2}H magnetic relaxation dispersions (MRD) were measured for the V66E and V66K mutants of Staphylococcal nuclease. In unmutated Staphylococcal nuclease, glutamic acid and lysine residues were buried in predominantly apolar environments. At neutral pH, where these residues were uncharged, no evidence of buried water molecules was found near the mutation site for V66E and V66K. This contrasted with a previous cryogenic crystal structure of the V66E mutant, but was consistent with the room-temperature X-ray crystal structure of V66E reported here. MRD measurements at different pH values indicated that ionization of Glu-66 or Lys-66 was not accompanied by penetration of long-lived water molecules. On the other hand, the MRD data were consistent with a local conformational change in response to ionization of the internal residues.

TRULOVE, Paul C., Assistant Professor, (co-author), "Improved Thermal Stability of Organically Modified Layered Silicates**,"** *Clay and Clay Minerals*, Vol. 52, No. 2, pp. 171 – 179, 2004.

Bromide-containing impurities were found to decrease the thermal stability of quaternary alkyl ammonium-modified layered silicates. Improved purification procedures completely removed bromide and led to a 20ºC to >100ºC increase in organic modified layered silicate thermal stability. Using mass spectrometry and thermal and electrochemical analysis, N,N-dimethyl-N,N-di octadecyl quaternary ammonium-modified montmorillonite and fluorinated synthetic mica were found to degrade primarily through elimination and nucleophilic attack by these anions. The nature of residual bromides was identified and quantified, and the efficiency of removing these anions was found to be solvent dependent; sequential extraction, first ethanol then tetrahydrofuran, gave the best results. This exhaustive extraction method represents a viable alternative to the use of expensive, more thermally stable oniumion treatments for layered silicates.

WHITAKER, Craig M., Associate Professor, (co-author), "Tuning Current Rectification Across Molecular Junctions," *Nanotechnology*, Vol. 15, pp. S489-S493, 2004.

The ability to tune the current rectification in metal-molecule-metal junctions through control of the interaction strength of one of the two metal-molecule contacts was demonstrated. Current-voltage characteristics of thiolate bound molecular wires with a nitro or pyridine termination show that the extent of current rectification in a molecular junction correlates well with the extent of coupling between the chemical linker and metal electrode.

Conference Proceedings

CHEEK, Graham T., Professor, and SANDERS, Eli, Midshipman 1/C, USN, "Electrochemical Investigations of Lewis Acid Interactions with Ketones in a Room-Temperature Ionic Liquid," *Proceedings of the Electrochemical Society 2004 Molten Salt Symposium*, accepted for publication.

The voltammetric behavior of fluorenone in the room-temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) has been studied. As in acetonitrile, two successive one-electron transfers were observed, although the second process is less reversible in EMIBF4 than in acetonitrile. Addition of BF_3 etherate produces an additional reduction peak at more positive potentials, indicative of complexation of fluorenone by BF_3. Upon addition of aluminum chloride to the melt, formation of chloride is indicated, probably by interaction with the BF_4^- anion. Complexation of fluorenone still occurs, however, implying that aluminum chloride is converted to another species, possibly BF_3, in this process.

CHEEK, G.T., Professor, (co-author), "Electrochemical Reduction of TiO_x at Room Temperature in Ionic Liquids," *Proceedings of the Electrochemical Society 2004 Molten Salt Symposium*, accepted for publication.

The reduction of the surface oxide formed on the surface of the Ti metal on heat treatment has been a long-standing research problem. In this paper, the results on efforts to reduce the oxide on Ti using the room-temperature molten salt system $AlCl_3$: 1-ethyl-3-methylimidazolium chloride are presented. After cycling the potential several times between +0.5 V and -1.6V (vs Al in 1.5:1.0 acidic melt), a well-developed anodic peak at -0.5 V was observed, suggesting reduction of the TiO_2 to Ti metal, with subsequent oxidation at -0.5V. Holding the potential at -1.6V for 15 minutes produced an even larger anodic peak at -0.5V, providing further evidence for reduction of TiO_2 to Ti at -1.6V.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-authors), "Application of Trialkylimidazolium Liquids and Salts to the Preparation of Polymer – Layered Silicate Nanocomposites and Polymer – Carbon Nanotube Nanocomposites," ACS Symposium Series, No. 913, in press.

> Polymer – layered silicate and polystyrene – carbon nanotube nanocomposites have been prepared via melt-blending. The thermal stability was analyzed using thermal gravimetric analysis and the extent of nanoparticle dispersion has been examined using powder x-ray diffraction (XRD) and transmission electron microscopy (TEM). Phase behavior of polystyrene nanocomposites was characterized using differential scanning calorimetry (DSC). The imidazolium salts used in this study were found to greatly expand the gallery d-spacing of montmorillonite to produce nanocomposites with a predominantly intercalated structure and to greatly improve the dispersion of MWNT in polystyrene to produce polymers with superior

O'SULLIVAN, D. W., Associate Professor, (co-author), "Photochemical Production of H_2O_2 and Chromophoric Dissolved Organic Matter Changes in Coastal Waters", *Proceeding for the Mediterranean Conference on Chemistry of Aquatic Systems*, Reggio Calabria, Italy, September 2004, pp. OC10.

> The photochemical production of hydrogen peroxide (H_2O_2) has been observed in many natural waters. Because hydrogen peroxide can act as an oxidant and reductant, it participates in an extensive suite of reactions in surface waters. Hydrogen peroxide is produced as a secondary photochemical product of chromophoric dissolved organic matter (CDOM) photolysis. The photochemical production of H_2O_2 was examined in relation to measures of changes in CDOM optical properties during laboratory irradiations of coastal waters with varying levels of CDOM. CDOM optical property changes were characterized by changes in CDOM absorbance and synchronous fluorescence. Apparent quantum yields for the photochemical production of hydrogen peroxide were determined in laboratory irradiations of filtered surface waters from several locations in the Chesapeake Bay and in Arctic coastal waters with varying levels of CDOM. The apparent quantum yield for H_2O_2 decreases with increasing wavelength from 280 nm to 500 nm, the majority of H_2O_2 production occurs at wavelengths less than 340 nm. The apparent quantum yield for H_2O_2 production at 290 nm ranged from 4.2×10^{-4} to 2.1×10^{-6} mol einstein^{-1} from fresh to marine waters. A linear relationship was found between the production of H_2O_2 and change in CDOM absorbance characterized as photobleaching, loss of absorbance. Apparent Quantum yields for hydrogen peroxide production and CDOM photobleaching were decoupled for the same water samples. Methylhydroperoxide (CH_3O_2H) was the only short chain organic peroxide produced during the irradiations, and its production was about an order magnitude less than that of hydrogen peroxide. Peroxide production was greatest in waters containing significant amounts of terriginous C in the form of humic substances. The relationship between the production of peroxides and changes in synchronous fluorescence, and CDOM chemical changes characterized by dissolved organic carbon production were examined. No significant relationship was observed between DOC production and peroxide production. The affects of changes in salinity on peroxide production efficiency were determined in relation to CDOM optical property changes for fresh water CDOM isolated from the Elizabeth River, VA. Photochemical production of H_2O_2 changed as Elizabeth River CDOM experienced different salinity conditions.

Book Chapters

BENDLER, John T., Professor (USNA Physics Department), and SCHROEDER, Maria J., Associate Professor, (co-authors), "Synthesis of 1,1-Dichloro-2-2-bis[4-(4'-Hydroxyphenyl)phenyl]ethene and its Incorporation into Homo- and Heteropolycarbonates," D. J. Brunelle and M. R. Korn (editors), Advances in Polycarbonates, American Chemical Society Press, Washington, D. C., pp. 133-146, 2005.

> Since their discovery over fifty years ago, polycarbonates have been utilized in a number of applications from optical recording media (CD, DVD) to automotive parts. Their versatility as engineering materials stem from their high glass transition temperatures, exceptional strength, and optical transparency, however problems with their synthesis and processing have always existed. The military is currently investigating the development of new polycarbonate-based materials and nanocomposites for use in transparent armor

and coatings applications. In this work, a new monomer analog of 1,1-dichloro-2,2-bis-(4-hydroxyphenyl)-ethylene (BPC) was synthesized with a higher aspect ratio than BPC. This monomer was polymerized into polycarbonates exhibiting improved ductility and heat-resistance. In addition, the monomer 1,1-dichloro-2,2-bis[4'-4-hydroxyphenyl)phenyl]ethene (TABPC) was synthesized with homopolycarbonates and heteropolycarbonates of TABPC subsequently polymerized. Structures were confirmed by infrared and NMR spectroscopic analyses. Characterization information, such as molecular weight distributions and glass transition temperatures, was also obtained to confirm the potential of these new polycarbonate-based materials in engineering applications.

ELERT, Mark L., Professor, Zybin, S. V., and White, C. T., "Shock-Induced Chemistry in Hydrocarbon Molecular Solids," in *Chemistry at Extreme Conditions*, M. R. Manaa, ed., Elsevier, 2005.

Shock waves produced by an impact cause a transient pulse of high pressure and high kinetic energy as they propagate through condensed phases. The products and reaction mechanisms of shock-induced chemical reactions may therefore be quite different than those produced under ambient conditions or static high pressure. An understanding of shock-induced chemistry is of great importance in several disciplines. One obvious example is the reaction chemistry of high explosives. Another is the chemical response of common materials such as ceramics and metal alloys which may be subjected to shock waves due to proximity to an explosive device. It is also of significant interest to the astrophysical community to understand the chemical reactions which might be induced by shock impact of comets or meteorites into planetary atmospheres. In this regard, the shock-induced chemistry of molecular hydrocarbons is of particular interest because of their central role in the development of life, and the ubiquity of small hydrocarbons such as methane in the atmospheres of many planetary bodies.

The challenges facing any experimental time-resolved study of shock-induced chemistry are significant due the extremely short time scales involved and the potentially destructive nature of the shock wave itself. These reactions can, however, be studied by the technique of molecular dynamics simulations. Some recent molecular dynamics studies of shock-induced chemistry in condensed-phase hydrocarbon systems are summarized in this report.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-authors), "Thermal and Kinetic Studies of Trialkylimidazolium Salts," in Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities, Robin D. Rodgers and Kenneth R. Seddon, Eds.; ACS Symposium Series No. 902, The American Chemical Society, in press.

The thermal properties of trialkylimidazolium room temperature ionic liquids (RTILs) have been determined using a flashpoint apparatus and the technique of thermal gravimetric analysis (TGA). Using a Setaflash flashpoint analyzer, all the salts studied were found to have flashpoints above 200ºC. TGA was utilized to study the decomposition of imidazolium based RTILs. The effects of C-2 hydrogen substitution, structural isomerism, alkyl chain length, anion type, and purge gas type is discussed. The decomposition kinetics of 1,2-dimethyl-3-butylimidazolium hexafluorophosphate was investigated using TGA. The global kinetic model and TGA Arrhenius parameters have been determined by employing both constant heating rate and isothermal programs.

HARRISON, J.A**.,** Professor, (co-author), "Computational Modeling of Nanometer-Scale Tribology", in *Introduction to Nanotribology and Nanomechanics*, Ed. by B. Bhushan, Chapter 13, Springer-Verlag, Heidelberg, Germany, 2005, in press.

HARRISON, J.A**.,** Professor, (co-author), "Computer Simulations of Nanometer-Scale Indentation and Friction", in the *Handbook on Nanotechnology*, 2nd Edition, Ed. B. Bhushan, Springer-Verlag, Heidelberg, Germany, in press.

LIN, Shirley, Assistant Professor, (co-author), "Isotactic Polypropylene from C_2- and pseudo-C_2-Symmetric Catalysts," Catalysis for Stereoregulating Polymerization, Boca Raton: CRC Press, in press.

Polypropylene is one of the most highly utilized engineering plastics with production in the United States and Canada of over 8 million metric tons in 2003. The vast majority of polypropylene sold is isotactic polypropylene (iPP), a resin valued for its strength, toughness, chemical and heat resistance, and processability. The highly stereoregular structure of iPP, in which the pendant methyl groups reside on the same side of the polymer chain, allows the material to have a high melting point. A versatile plastic, iPP can be found in a wide range of applications from packaging to fibers to containers.

Commercial, highly crystalline iPP is largely synthesized using traditional heterogeneous Ziegler-Natta catalysis but the advent of homogeneous group 4 metallocenes has enabled polyolefin producers to access a wider range of polymer microstructures and properties. The mechanism of stereospecific polymerization by these catalysts is now well-understood; the issues of stereocontrol and influence of the metallocene catalyst structure on the propylene polymerization behavior have been discussed in detail in previous reviews. Excellent review articles are also available on the synthesis of chiral group 4 metallocenes. This chapter will focus upon the details of how the C_2-symmetry of the catalyst is exploited in the synthesis of iPP and then survey the general ligand structures that are commonly encountered.

TRULOVE, Paul C., Assistant Professor, (co-author), "Surface Chemistry and Tribological Behavior of Ionic Liquid Boundary Lubrication Additives in Water," in Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities, Robin D. Rodgers and Kenneth R. Seddon, Eds.; ACS Symposium Series No. 902, The American Chemical Society, in press..

Ionic liquids have been intensely studied regarding their properties as an environmentally friendly solvent. Conversely, little work in the field of tribology has been accomplished to date. Ionic liquids posses many favorable properties that would suggest that they have significant potential for use in the tribology field. One area that is discussed here is the use of ionic liquids as a boundary lubricant additive for water. The chemical and tribochemical reactions that govern their behavior were evaluated for two ionic liquids. Under water lubricated conditions, silicon nitride ceramics exhibit a characteristic running in period of high friction, through which surface smoothing and tribochemical reactions lead to low friction coefficients. The running-in period of high friction is the period where the majority of the wear occurs. The use of a suitable boundary lubricant to reduce the running-in period could be of significant importance. A promising candidate for this application is ionic liquids. We present the affects that ionic liquids have on the friction and wear properties of Si_3N_4 in particular the affects on the running-in period. Tribological properties were evaluated using a pin-on-disk and reciprocating tribometers. Solutions containing 2 wt % ionic liquids were produced for testing purposes. Chemical analysis of the sliding surfaces was accomplished with x-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR). The test specimens were 1" diameter Si_3N_4 disks sliding against ¼" Si_3N_4 balls. The use of ionic liquids as a boundary lubricant additive for water resulted in dramatically reduced running-in periods for silicon nitride from thousands to the hundreds of cycles. Proposed mechanisms controlling the friction and wear include the formation of a transfer film and the inception of an electric double layer.

TRULOVE, Paul C., Assistant Professor, and FOX, Douglas M., Assistant Research Professor, (co-authors), "The Application of Trialkyl-Imidazolium Ionic Liquids and Salts for the Preparation of Polymer-Clay Nanocomposites," in Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities, Robin D. Rodgers and Kenneth R. Seddon, Eds.; ACS Symposium Series No. 902, The American Chemical Society, in press.

Increasing the thermal stability of organically modified layered silicates (clays) is essential for the application of polymer-clay nanocomposites on the industrial scale. Trialkyl-imidazolium ionic liquids and salts were investigated as more thermally stable alternatives to the current alkyl ammonium clay treatments. Imidazolium treated montmorillonite clays were prepared by ion exchange and their thermal stabilities and structural properties evaluated. Tri-imidazolium treated clays were also melt blended with polystyrene (PS) and poly(ethylene terephthalate) (PET) to form nanocomposites. Results showed that the imidazolium

treated clays have significantly higher thermal stabilities than current clay treatments, and they exhibit excellent compatibility with PS and PET.

Presentations at Professional Meetings and Conferences

CHEEK, Graham T., Professor, and SANDERS, Eli, Midshipman 1/C (USN), "Electrochemical Investigations of Lewis Acid Interactions with Ketones in a Room-Temperature Ionic Liquid," Electrochemical Society 206th Meeting, Honolulu HI, 9-14 October 2004.

CHEEK, Graham T., Professor, and O'Grady, William E., "Electrochemical Determination of Water Content in a Room-Temperature Ionic Liquid," Electrochemical Society 207th Meeting, Québec, Canada, 15-20 May 2005.

FERRANTE, Robert F., Professor, Moore, Marla H., and STONE, Jason, Midshipman 1/C (USN), "IR Studies of Ammonia Hydrates: Effects of Thermal and Radiation Processing", 35th Scientific Assembly of the Committee on Space Research (COSPAR), Paris, France, 18-25 July 2004.

FERRANTE, Robert F., Professor, Moore, Marla H., STONE, Jason, Midshipman 1/C (USN), and Hudson, Reggie L., "IR Studies of Ammonia Hydrates", 36th Annual Meeting of the Division of Planetary Sciences, American Astronomical Society, Louisville, KY, 8-12 November 2004.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-presenters), "The Use of Imidazolium Based Ionic Liquids for the Preparation of Polymer – Layered Silicate and Polymer – Carbon Nanotube Nanocomposites," EUCHEM 2004 Molten Salts Conference, Piechowice, Poland, 20-25 June 2004. (Invited presentation)

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-presenters), "Processing of *Bombxy mori* Silk Using Ionic Liquids," 14th International Symposium on Molten Salts, 206th National Electrochemical Society Meeting, Honolulu, HI, 3-8 October 2004.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-presenters), "Preparation of Homogeneously Dispersed Trialkyl Imidazolium Compatilized Multi Walled Carbon Nanotube/Polystyrene Nanocomposites via Melt Extrusion," 14th International Symposium on Molten Salts, 206th Meeting of the Electrochemical Society, Honolulu, HI, 3-8 October 2004.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-presenters), "Decomposition Kinetics of 1-Butyl-2,3-Dimethylimidazolium Tetrafluoroborate and the Effects of Impurities Using TGA," 14th International Symposium on Molten Salts, 206th Meeting of the Electrochemical Society, Honolulu, HI, 3-8 October 2004.

FOX, Douglas M., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-presenters), "The Use of 1,2-Dimethyl-3-(Benzyl Ethyl Iso-butyl-POSS)imidazolium Chloride as an Organic Modifier in Polymer – Layered Silicate Nanocomposites," 14th International Symposium on Molten Salts, 206th Meeting of the Electrochemical Society, Honolulu, HI, 3-8 October 2004.

GANN, Jami L., Midshipman 1/C, (USN) and URBAN, Joseph J., Associate Professor, "Computational Studies of Fluorinated Amino Acids," 229th National Meeting of the American Chemical Society, San Diego, CA, 13-17 March 2005.

GUTTERIDGE, Clare E., Assistant Professor, "Chalcone Synthesis, Quarterly Review," Walter Reed Army Institute of Research, MD, 26 August (Quarterly), 22 September (Annual) and 2 December (Quarterly) 2004.

GUTTERIDGE, Clare E., Assistant Professor, "Chalcone Synthesis, Quarterly Review," Walter Reed Army Institute of Research, MD, 10 March and 2 June 2005.

HARRISON, Judith A., Professor, "Molecular Dynamics Simulations of Nanocomposite Diamond-like Carbon", MURI Review, Wright Patterson Air Force Base, Dayton, OH, 23-24 May 2005.

HARRISON, Judith A., Professor, "The Tribology of Carbon, Hydrogen, and Silicon-containing Solid Lubricants", The Annual Meeting of The Society of Tribologists and Lubrication Engineers (STLE), Las Vegas, NV, 15-18 May 2005. (Invited speaker)

HARRISON, Judith A, Professor, "Contact Forces between an AFM-like Tip and Model Self-Assembled Monolayers", The University of New Hampshire, Durham, NH, 21 April 2005. (Invited speaker)

HARRISON, Judith A., Professor, "The Elucidation of Atomic-Scale Friction at Amorphous Carbon Interfaces using MD Simulations", 107th Annual Meeting of the American Ceramic Society, Baltimore, MD, 10-13 April 2005. (Invited speaker)

HARRISON, Judith A., Professor, MIKULSKI, P. T., Assistant Professor (USNA Physics Department), CHATEAUNEUF, G. M., Assistant Research Professor, SCHALL, J. D., Assistant Research Professor, and GAO, G, Assistant Research Professor, "Carbon, Hydrogen, and Silicon-containing Solid Lubricants", American Physical Society March Meeting, Los Angeles, CA, 21-25 March 2005. (Invited contribution)

HARRISON, Judith A., Professor, "Atomic-Scale Tribology of Solid Lubricants", Fall Meeting of The Materials Research Society, Boston, MA, 29 November - 3 December 2004. (Invited speaker)

HARRISON, Judith A., Professor, "The Molecular-Scale Tribology of Solid Lubricants for MEMS Applications: Molecular Dynamics Studies", AFOSR Tribology Review, Annapolis, MD, 3-5 November 2004.

HARRISON, Judith A., Professor, "Multi-functional Extreme Environment Surfaces: Thrust Area II: Cryogenic and Space Applications", AFOSR Tribology Review, Annapolis, MD, 3-5 November 2004.

HARRISON, J. A., Professor, (co-presenter), "A Hybrid Atomistic/Continuum Method Applied to Fluid Flow and Solid Contact, American Physical Society March Meeting, Los Angeles, CA, 21-25 March 2005. (Invited contribution)

HARRISON, J. A., Professor, (co-presenter), "Contact and Friction between Rough Surfaces at the Nanometer Scale", Fall Meeting of The Materials Research Society, Boston, MA, 29 November - 3 December 2004.

HARRISON, J. A., Professor, (co-presenter), "From Atomic Scale Dynamics to Macroscopic Friction Laws", International Tribology Conference, Kobe, Japan, 30 May -2 June 2005. (Invited contribution)

HENDERSON, Wesley A., Assistant Research Professor, and TRULOVE, Paul C., Assistant Professor, (co-presenters), "Physical Properties of Ionic Liquid-LiX Mixtures," 207th Meeting of the Electrochemical Society, Quebec City, Quebec Canada, 15 – 20 May 2005.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "INTEX/ICART Hydrogen Peroxide and Methylhydroperoxide Measurements and Intercomparison", *ICART Science Team Meeting*, Pease, NH, 23 July 2004.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "Photochemical Production of H_2O_2 and Chromophoric Dissolved Organic Matter Changes in Coastal Waters", *Mediterranean Conference on Chemistry of Aquatic Systems*, Reggio Calabria, Italy, 5 September 2004.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "Hydrogen Peroxide and Methylhydroperoxide Measurements during RICO", Operations Center, Antigua, WI, 21 January 2005.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "Peroxide and Formaldehyde Observations during INTEX-A", NASA INTEX-A Data Workshop, Norfolk, VA, 29 March 2005.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "Preliminary Observations of Methylhydroperoxide (CH_3OOH) and Formaldehyde (CH_2O) in Fresh Convective Outflow during INTEX-NA, summer 2004", *EOS Transactions American Geophysical Union*, 85(47) Fall Meeting 2004.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "Airborne Formaldehyde Measurements during INTEX-A: A Preliminary Look at Mixing Ratio Distributions over North America", *EOS Transactions American Geophysical Union*, 85(47) Fall Meeting 2004.

O'SULLIVAN, D. W., Associate Professor, (co-presenter), "Observations and Preliminary Interpretation of Hydrogen Peroxide (H_2O_2) and Peroxyacetic acid (PAA) in the Atmosphere during INTEX-NA, summer 2004", *EOS Transactions American Geophysical Union*, 85(47) Fall Meeting 2004.

REHILL, Brian J., Assistant Professor, "All Leaves are Not Created Equal: How Developmental Differences in Plant Chemistry Affect Herbivores and Communities", University of Maryland-Baltimore County, Baltimore, MD, 7 October 2004. (Invited speaker)

REHILL, Brian J., Assistant Professor, (co-presenter), "Pemphigus, Cleavage, and Targets," 3rd Annual Cottonwood Research Conference, Northern Arizona University, Flagstaff, AZ, 14 – 16 March 2005.

ROA, Nicholas A., Midshipman 1/C (USN), and COPPER, Christine L., Associate Professor, (co-presenters), "Effect of Functional Group Type on Sol-Gel Capillary Electrochromatography", PittCon 2005, Orlando, FL, 28 February - 3 March 2005.

SCHLESSMAN, Jamie, Assistant Professor, (co-presenter), "Molecular Determinants of p*K*a Values of Ionizable Residues Involved in Clusters and Networks: Contributions by Short-range Interactions and by Local Conformational Fluctuations." Biophysical Society Meeting, Long Beach, CA, 12-16 February 2005.

SCHROEDER, Maria J., Associate Professor, and FONTANELLA, John J., Professor (USNA Physics Department), (co-presenters), "Evolution of the Dynamics of 1,4-Polyisoprene: Dielectric Spectroscopy Measurements of a Glass-Former," 229th National Meeting of the American Chemical Society, San Diego, CA, 13-17 March 2005.

STANLEY, John T., Midshipman 1/C (USN), DILLNER, Debra K., Associate Professor, LIN, Shirley, Assistant Professor, and Traficante, Daniel, "Carbon-13 Chemical Shift Correlations: Benzaldehydes and Acetophenones", 229th ACS National Meeting, San Diego, CA, 13-17 March 2005.

TEICHERT, Erika M.., Midshipman 1/C (USN), and COPPER, Christine L., Associate Professor, (co-presenters), "Optimization of Gel Porosity in Sol-Gel Capillary Electrochromatography", PittCon 2005, Orlando, FL, 28 February - 3 March 2005.

TILLMAN, Brendon G., Midshipman 1/C, (USN) and URBAN, Joseph J., Associate Professor, "Computational Studies of Fluoroolefins as Peptide Mimetics," 229th National Meeting of the American Chemical Society, San Diego, CA, 13-17 March 2005.

TRULOVE, Paul C., Assistant Professor, and FOX, Douglas M., Assistant Research Professor, (co-presenters), "The Use of Molten Salts for the Preparation of Novel Polymer Nanocomposites," EUCHEM 2004 Molten Salts Conference, Piechowice, Poland, 20-25 June 2004. (Invited presentation)

URBAN, Joseph J., Associate Professor, "Computational Evaluation of Stereoelectronic Effects in Fluorinated Amines," 228th National Meeting of the American Chemical Society, Philadelphia, PA, 22-26 August, 2004.

WAITE, Boyd A., Professor, "The Impact of Multiple Exposure and Accountability for Learning from Laboratory Experiences," McGraw-Hill Symposium on General Chemistry, Tuscon, AZ, 27-30 January 2005.

WHITAKER, Craig M., Associate Professor, "Organic Materials for Photovoltaic Applications, Rodcoils and BuckyBombs," Naval Surface Warfare Center, Indian Head, Synthesis Division, Indian Head, MD, 13 January 2005. (Invited speaker)