Division of Mathematics and Science

CAPT William C. Ostendorff, USN
Director

Chemistry Department

Professor Boyd A. Waite
Chair

This past year was very successful in terms of external recognition of research accomplishments within the Chemistry Department. Associate Professor Judith Harrison continues to develop an international reputation in the emerging field of tribology, and has supported two post-doctoral associates within the department. Professor Mark Elert also hosted a post-doctoral associate who studied molecular simulations of detonation reactions. Associate Professor Mark L. Campbell continued with funding through the prestigious Henry Dreyfus Teacher/Scholar Award (one of five nation-wide), providing funding for his own research and for the department. Associate Professor Roy E. McClean was awarded the Kinnear Fellowship at the U.S. Naval Academy in support of his work in experimental physical chemistry. Assistant Professor Daniel W. O'Sullivan did field work in the South Pacific as part of his NASA-funded research in the field of atmospheric chemistry. Professor Robert F. Ferrante served as principle adviser to Midshipman 1/C Robert M. Gallagher, an Aerospace Engineering major, the 2001 recipient of the Harry E. Ward Prize for the outstanding Trident Scholar project.

The Chemistry Department faculty and midshipmen chemistry majors are supported by a diverse array of state-of-the-art instrumentation and computational facilities. Ten different midshipmen participated in directed research courses. Several of the midshipmen attended national scientific meetings and presented results of their work during the year.

The Chemistry Department faculty has continued to pursue collaborative research efforts with Navy laboratories and other government and private institutions. This year faculty collaborated with projects at the Naval Research Laboratory (NRL), the National Aeronautics and Space Administration (NASA), and the Johns Hopkins University. Faculty members were supported by grants from the Air Force Office of Scientific Research (AFOSR), NASA, the Office of Naval Research (ONR), the Petroleum Research Fund (PRF), the National Science Foundation (NSF), and the Research Corporation.

Other research interests of the faculty include: organic synthesis of species for methanol fuel cells, radio-isotope studies in connection to specialized medical scanning technology, detonation simulations, electrochemical studies of fused salts, development of analytical methods based on electrophoretic techniques, synthesis and characterization of organic and organo-metallic species, the effects of chemical agents in atmospheric chemistry, and the biochemical functional analysis of protein folding, among others. The active involvement of both civilian and military faculty in research provides strength to the curriculum and helps prepare our chemistry graduates for the technical challenges awaiting them in the fleet.

Sponsored Research

Kinetics of Gas Phase Oxidation Reactions of Transition Metal Atoms with Oxygen Containing Oxidants

Researcher: Associate Professor Mark L. Campbell
Sponsor: The Camille and Henry Dreyfus Foundation

The objective of this research is to determine the rate constants for reactions of ground state and low-lying excited state transition metal atoms in the gas phase with oxygen-containing oxidants as a function of temperature and pressure. In particular, three projects are in varying stages of completion: (1) reactions of transition metals with N_2O, (2) reactions of ground state and low-lying excited states of niobium and tantalum with several oxidants, and (3) reactions of zirconium and hafnium with water. By obtaining Arrhenius parameters for these reactions, geometric factors and energy barrier effects are determined. The experimentally measured rate constants and barriers are analyzed to determine if a relationship exists between these values and the physical properties of the transition metals and reactants. Results for the reactions with N_2O are then compared to the calculated values from a theoretical model developed by Fontijn and co-workers. The reactions of niobium and tantalum indicate the

importance electronic effects have on the reaction rate. The reactions of zirconium and hafnium with water will yield a better understanding of chemical reactions that may occur during accidents in nuclear reactors. Completion of this research will greatly enhance our understanding of transition metal chemical reactions.

Electrochemical Studies of the Fries Rearrangement in a Room-Temperature Molten Salt

Researcher: Professor Graham T. Cheek
Sponsor: 2000 Kinnear Fellowship

The Fries rearrangement, in which a phenolic ester becomes an aromatic ketone, is typically carried out in the presence of a Lewis acid catalyst. This observation suggests that solvent systems containing aluminum chloride may be profitably used for studying this reaction. In the present work, the aluminum chloride: 1-ethyl-3-methylimidazolium chloride (EMIC) molten salt system has been used as a medium in which to study the Fries rearrangement of phenyl benzoate. Since the melt acidity can be varied over many orders of magnitude by changing the relative proportions of aluminum chloride and EMIC, this solvent system provides an excellent opportunity for studying the effect of Lewis acidity on the course of the reaction.

The reduction of phenyl benzoate in the basic melt (with a molar excess of EMIC) occurs at -1.86 V. No rearrangement was found to occur even at elevated temperatures. As $AlCl_3$ is added to the system to give only a slight molar excess of $AlCl_3$, a shift in the reduction process to -0.78 V occurs. The interaction of the catalyst with the substrate, then, can be easily observed by electrochemical measurements. The progress of the reaction under slightly acidic conditions was followed by monitoring the decrease in peak current at -0.78 V (complexed ester peak), and the appearance of another peak at -1.20 V (reaction product). The reaction was found to be complete after several days at 80oC, and aqueous workup/solvent extraction confirmed production of the hydroxy-benzophenone rearrangement products. It was thought worthwhile to study the reaction in the neutral buffered melt as well. Under these conditions, reduction of phenyl benzoate occurred at -0.83 V, similar to the potential found in the acidic melt. Reaction characteristics were also similar, requiring three or four days at 75°C for completion. The rearrangement products were formed in good yield, giving 4-hydroxybenzophenone as major product and lesser amounts of the 2-hydroxy-benzophenone isomer. Crossover experiments with benzene added to the neutral buffered melt gave only a minimal amount of benzophenone (cross-over product), indicating either that the pathway is intramolecular or that benzene is not sufficiently active to take part in the reaction.

Isolation And Characterization Of Metabolic Intermediates From Polycyclic Aromatic Hydrocarbon (PAH) Biodegradation

Researcher: Associate Professor Christine L. Copper
Sponsor: Dr. John H. Callahan, Section Head/Research Chemist, Chemical Dynamics and Diagnostics Branch, Chemistry Division, Analytical Chemistry Section (Code 6115)

Capillary electrophoresis (CE) and mass spectrometry (MS) were optimized for analysis of compounds that are known metabolites of biodegradation. The PAH degrading bacteria known as EPA 505 S. paucimobilus was employed in PAH biodegradation experiments performed in static or dynamic systems. Samples from these systems were screened for PAH metabolites using CE and MS methods. The presence of various known metabolites was confirmed and a structure of a previously unidentified metabolite of the PAH fluoranthene was proposed based on CE and MS results. Identification of this metabolite, which appears early in the degradation process, provides an important marker for factors that influence initial degradation steps. Work on this project continues and a publication containing a full report of the project will be completed this summer.

Capillary Electrophoresis as a Method for Ozone Determination in Atmospheres

Researcher: Associate Professor Christine L. Copper
Sponsor: Dr. John H. Callahan, Section Head/Research Chemist, Chemical Dynamics and Diagnostics Branch, Chemistry Division, Analytical Chemistry Section (Code 6115)

Capillary electrophoresis (CE) is used to quantify nitrate and nitrite extracted from nitrite-impregnated glass fiber filters (IGFF) that are used to monitor ozone in atmospheres (specifically submarines). The amount of nitrate produced from

conversion of nitrite in the filters is directly related to the amount of ozone passed over the filter. Results from CE analyses of the filters are compared to ion chromatographic (IC) analyses and indicate that analysis time, cost, and waste production are lower when the CE method is used. Work on this project continues and a publication containing a full report of the project will be completed this summer.

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

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

We propose the development of new nanocomposite oxygen-reduction catalysts designed for high catalytic activity plus high electron and proton transport. With this approach, we anticipate that the oxygen-reduction reaction will be improved, increasing the efficiency of PEMFCs. Furthermore, the amount of platinum in fuel cell cathodes will 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 will resolve whether the active catalyst is a Pt-Fe alloy or Pt-FeO_xH_y composite. The stability of the Pt-Fe systems will also be examined in the acidic and oxidizing conditions of the PEMFC cathode.

Platinum-free nanocomposite catalysts will be 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, will 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 $CaMoO_3$ and $SrCrO_3$, the conductivity of the electrodes will not be limited by electron transfer. The materials will be evaluated for stability under acidic and oxidizing conditions.

These catalysts will be provided to the Department of Energy fuel cell testing facility at the Los Alamos National Laboratory for characterization under fuel-cell operating conditions.

Investigations of Ionic Liquid Polymer Gel Electrolytes

Researcher: Major Hugh C. De Long, USAF (Assistant Professor at USNA)
Sponsor: Naval Research Laboratory (NRL)

Room-temperature ionic liquids composed of perfluoroanions and 1,3- dialkylimidazolium and 1,2,3-trialkylimidazolium 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. We are 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.

Investigations of Novel Nanocomposities Using Room Temperature Molten Salts

Researcher: Major Hugh C. De Long USAF (Assistant Professor at USNA)
Sponsor: Air Force Office of Scientific Research (AFOSR)

Room-temperature ionic liquids composed of perfluoroanions and 1,3- dialkylimidazolium and 1,2,3-trialkylimidazolium cations possess a number of unique properties that make them ideal electrolytes for nanocomposite work. In particular, they are nonflammable, nonvolatile, and chemically inert, and they intercalate into layered materials which makes them ideally suitable for our nanocomposites using clays. Also, unlike room-temperature ionic liquids based on chloroaluminate anions, these perfluoroanion electrolytes are not moisture sensitive. In this program, we are investigating the preparation and analysis of mica-type clays nano-dispersed in polymers. These "nanocomposites" exhibit the unusual combination of reduced flammability, in the form of lower peak heat release rates, and improved physical properties. The most significant aspect of the nanocomposite approach is the combined improvement in both flammability properties and physical properties. The key to successful generation of fully dispersed polymer-clay nanocomposites is the organic treatment used to prepare the clay silicate layers. Chemical compatibility of the organic treatment with the polymer is critical to producing fully optimized nanocomposites. In addition, the high thermal stability of these organic treatments is essential if melt processing methods are to be employed. In this program, we are developing novel organic treatments for clay-polymer nanocomposites. We are synthesizing unique imidazolium based salts, which possess both high temperature stability and tailorable polymer compatibility. We are using modern analytical methods, such as TEM, SEM, x-ray diffraction, NMR, TGA, TMA, and cone calorimeter, to characterize the physical and chemical properties of the salts, the treated clays, and the polymer nano-composites.

Modeling of Orientation Dependence of Shock Wave Properties in a Diamond Crystal

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

A series of molecular dynamics (MD) simulations using carbon reactive empirical bond order potentials was performed to study the orientation dependence of elastic-plastic and melting shock wave structure in a single diamond crystal. To study the fine-grained profiles of flow variables and their distribution functions, a previously developed special time-averaging technique was implemented within the shock reference frame. The calculated Hugoniot relations between shock and piston velocities as well as pressure and density show reasonable agreement with experiment. The shock waves propagating along the <100>, <110>, and <111> directions in diamond have a front structure similar to one in the Lennard-Jones fcc crystal studied previously: an elastic precursor with oscillatory structure exists in <110> and <111> shocks, while the <100> profile has not shown clear separation between elastic and plastic compression zones. Furthermore, for a given shock velocity, the shock-induced melting transition in <110> and <111> shocks differs from the <100> case where a metastable overheated state is developed behind the front. These effects could be explained by the orientation dependence of shear stress (large in the <110> and <111> cases and relatively small in <100> one).

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces

Researchers: Dr. Paul T. Mikulski (Post-Doctoral Fellow)
and Associate Professor Judith A. Harrison
Sponsor: The Air Force Office of Scientific Research (AFOSR)

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 have been used to investigate the atomic-scale origins of friction and wear in hydrocarbon systems. Previously, the atomic-scale friction that resulted when two diamond (111) surfaces are placed in sliding contact was examined. 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. We have used our re-fit potential energy function to examine the friction of n-alkane chains on diamond with different packing densities. (This potential energy function has been published in *The Journal of Chemical Physics*.) Simulations show that the tightly packed monolayers (or more ordered) have lower friction than the loosely packed (less ordered) monolayers in agreement with the experimental trend. The origin of this difference in friction appears to be related to differences in carbon-carbon bond-length distributions. These data have recently been accepted for publication in *The Journal of the American Chemical Society*. An analysis of system properties as they are related to friction appeared in *Tribology Letters*.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

Researchers: Dr. Guangtu Gao (Post-Doctoral Fellow)
and Associate Professor Judith A. Harrison
Sponsor: Office of Naval Research (ONR)

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, any 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. The phenomenon, called stiction, renders the MEMS device inoperable. Second, the wear rate of silicon is such that MEMS composed of silicon cannot be used in applications where 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.

A recently hired postdoctoral associate has examined the friction of amorphous carbon films on diamond as a function of film thickness. We find that the friction is independent of film thickness. These results are in the process of being fully analyzed.

Department of Defense (DoD) Reactive Atomic-Scale Potential Molecular Dynamics (RASP-MD) For Computation and Prediction of Materials Properties

Researchers: Dr. John W. Mintmire and Dr. Carter T. White (NRL),
Dr. Brad L. Holian (Los Alamos National Laboratories)
Dr. Daniel H. Robertson (IUPUI), Professor Mark L. Elert (USNA),
Dr. Steven J. Stuart (Post-Doctoral Fellow), and Associate Professor Judith A. Harrison
Sponsor: Common HPC Software Support Initiatives

The overall goal of this project is to develop a scalable and portable suite of programs for MD simulations of materials of critical DOD interest using chemically realistic potentials. The planned software suite will be developed as a main set of MD programs that interface with the empirical potential routines via a custom application programming interface (API). A set of auxiliary routines will be constructed that implement the NRL-developed REBO and ES+EAM potentials and the Naval Academy-developed AIREBO potential using API.

Investigations into the Effects of Tripodal Ligands on Transition Metal Environments

Researchers: Associate Professor J.R. Hartman and Midshipman 1/C A.L. Kammier, USN
Sponsor: Petroleum Research Fund B of the American Chemical Society

Crown and cryptand ligands are useful for binding metal ions because the constrained nature of crown and cryptand ligands allows them to form metal-complexes in which the metal has unusual steric and electronic properties. Unfortunately, crowns and cryptands are difficult to prepare and purify, and hence expensive.

Podands (“many-armed” ligands) can act as either constrained ligands that form cryptand-like metal complexes or as unconstrained ligands that form cross-linked polymeric metal complexes. In the proposed research, the chemistry of a novel series of TREN-based tripodal ligands have been synthesized and are being studied to characterize their method of binding and to determine where they fit in the scale of preorganization that ranges from linear ligands to cryptands.

We have begun to study the binding properties of TREN-based podand ligands by comparing the properties of the metal complexes with a series of podands to those with the analogous linear ligands. We have chosen to focus initially on a series of aminopyridyl ligands. We have prepared the ligands and are currently studying the steric, electronic, and gas-phase-reactivity properties of copper(II) and nickel(II) complexes to determine if the tripod cavity is constraining the conformation of the metal ions.

Synthesis and Characterization of Dithienothiophene Derivatives for Electroluminescent Applications

Researcher: Associate Professor William. B. Heuer
Sponsor: Dr. O. K. Kim, Research Chemistry, Naval Research Laboratory (NRL)

Electroluminescent (EL) materials are used in the fabrication of light-emitting diodes (LED’s), which have many important technological applications, (*e.g.*, in flat-panel displays.) A number of promising organic light-emitting diodes (OLED’s) have already been fabricated by spin-coating multiple layers of electroactive/photoactive polymers onto optically-active, conductive substrates. Each chemically-distinct polymer layer in the device serves a different function (electron-transporter, emitter, hole-blocker, etc.) Our approach has been to incorporate these different functionalities into a single molecule, based upon the p-conjugated linker dithienothiophene (DTT). In addition to being a strong emitter, DTT has also been shown to be particularly effective in mediating electronic communication between appended substituent (donor and/or acceptor) groups. However, DTT also has a strong tendency toward aggregation through p-stacking interactions, which is known to adversely affect emitting properties of such materials. In order to address this problem, we have undertaken the synthesis of several alkyl- and aryl-substituted derivatives of DTT in hopes that adding additional bulky functional groups to the planar DTT core will inhibit undesirable chromophore aggregation within the films. Initially, a 3,5-dimethyl-substituted DTT derivative has been synthesized, and efforts are currently underway to accumulate enough of this material to proceed with the preparation of the 2,6-dialdehyde derivative of this compound, which is required for the ultimate preparation of desired donor/acceptor-substituted compounds. Low yields encountered in the synthesis of dimethyl-DTT most likely results from occurrence of competing reac-

tions involving activation of methyl substituents by strong base n-BuLi in the course of the synthesis. In order to circumvent this problem, synthesis of a corresponding 3,5-diphenyl-substituted analogue is also being pursued.

Synthesis of [C-11]L-159,884: A Radiolabeled, Nonpeptide Angiotensin II Antagonist for Angiotensin II, AT_1 Receptor Imaging

Researcher: Associate Professor Christopher M. Kinter
Sponsors: Naval Academy Research Council (NARC) and the Division of Nuclear Medicine and Radiation Health Sciences, The Johns Hopkins University

Angiotensin II (Ang II) plays a key role in the regulation of cardiovascular function. The octapeptide angiotensin II is produced from angiotensin I by a reaction involving the enzyme angiotensin converting enzyme (ACE). Ang II, through interaction with membrane receptors in various tissues, controls the constriction of vascular smooth muscle, modulation of glomerular filtration rates, and sodium retention. Through these effects Ang II plays a critical role in the regulation of blood pressure. In fact, antihypertensin drugs such as captopril, enalopril, and lisinopril function by preventing the formation of Ang II by inhibiting ACE. Despite the clinical usefulness of the ACE inhibitors they do suffer from problems such as poor oral availability and their short duration of action. Additionally, these drugs suffer from common side effects such as a dry cough and angioneurotic edema. Pharmaceutical companies have begun to pursue a more direct method of regulating blood pressure by developing Ang II antagonist. Studies have shown that there are at least two distinct Ang II receptor subtypes, AT_1 and AT_2. The first, AT_1, is thought to be responsible for all the known physiological function of Ang II. whereas, the functional role of the AT_2 receptors has yet to be clearly demonstrated. Research effort has been directed towards the synthesis of [C-11]L-159,884 a radiolabeled, nonpeptide angiotensin II antagonist that is useful in imaging the angiotensin II, AT_1, receptor using positron emission tomography (PET). L-162,914 serves as the precursor to [C-11]L-159,884 and was prepared by a convergent route in 11 steps with an overall yield of 34.4%. [C-11]L-159,884 was produced by methylation of the phenolic group of the precursor by cyclotron produced [C-11] methyl iodide. Studies of the angiotensin II AT_1 are currently underway using [C-11]L-159,884.

Synthesis of Radiotracers for the Study of the Nicotinic Acetylcholine Receptor

Researcher: Associate Professor Christopher M. Kinter
Sponsors: Naval Academy Research Council (NARC) and the Division of Nuclear Medicine and Radiation Health Sciences, The Johns Hopkins University

The endogenous cholinergic neurotransmitter, acetylcholine, exerts its biological effect via two types of cholinergic receptors: the muscarinic acetylcholine receptor (mAChRs) and the nicotinic acetylcholine receptors (nAChRs). Considerable effort has been directed at identification and characterization of ligands for nicotinic acetylcholine receptors. The interest in these compounds stems in part from evidence that agents acting at this receptor may have therapeutic utility in the treatment of a variety of central nervous system disorders including Alzheimer's and Parkinson's diseases, attention deficit or hyperactivity disorders, Tourette's syndrome and depression. Additionally, this receptor has been implicated in a variety of central processes such as learning, memory, and the relief of pain. Several potential compounds have been identified for use in the study of the nicotinic acetylcholine receptor and efforts have been directed towards their synthesis and radiolabeling with positron emitting isotopes.

Association Reaction Of Cobalt With Sulfur Dioxide

Researcher: Associate Professor Roy E. McClean
Sponsor: 2001 Kinnear Fellowship

The gas phase reaction kinetics of ground state Co with SO_2 are reported. The objective of this work was to measure rate constants as a function of temperature and total pressure. Such data provides information on the efficiency of 1:1 adduct formation in transition metal/SO_2 systems. This work also provides fundamental information on the importance of orbital occupancy in transition metal reactivity.

The laser photolysis/laser-induced fluorescence (LP/LIF) technique was used in this work. In brief, a stainless steel reactor contained $Co(C_5H_5)(CO)_2$, SO_2, N_2, and CO_2. CO_2 served as the bath gas, and N_2 served as the carrier of the $Co(C_5H_5)(CO)_2$

vapor to the reaction chamber. Co atoms were produced by the laser photodissociation of $Co(C_5H_5)(CO)_2$, after which, reaction occurred between the formed Co atoms and SO_2. Relative concentrations of Co atoms were monitored by LIF as a function of time. Reactions were carried out under pseudo-first order conditions where $[Co] << [SO_2] << [CO_2]$.

Experimental data were collected at 294, 398, and 498 K. At each temperature, rate constants were measured at various intervals between 5 and 40 Torr total pressure. Rate constants were found to be independent of temperature; however, they increased with increasing total pressure, indicating the following association reaction

$$Co + SO_2 + CO_2 \rightarrow CoSO_2 + CO_2$$

The third order rate constant is given by $k_o = 5.24 \times 10^{-31}$ cm^6 $molecule^{-2}$ s^{-1} (30% uncertainty). The Co + SO_2 reaction, when compared to more reactive systems such as Cr + SO_2, is inefficient and supports the argument that the orbital occupancy of transition metal atoms plays an important role in their reactivity. Ground state Co is of s^2 occupancy and ground state Cr is of s^1 occupancy; transition metal atoms with s^1 occupancies are generally more reactive than those of s^2.

The objectives of this work were achieved. Theoretical calculations are now being performed in order to obtain more fundamental information on the $CoSO_2$ adduct.

Hydrogen peroxide, methylhydroperoxide, and formaldehyde: Their Relationship To Tropospheric Oxidant Chemistry And Transport Over The Equatorial South Pacific

Researchers: Assistant Professor Daniel W. O'Sullivan, Co-PI
and Dr. Brian G. Heikes (PI; University of Rhode Island)
Sponsor: National Aeronautics and Space Administration (NASA)

Measurements of gas-phase hydrogen peroxide, methylhydroperoxide, and formaldehyde on board both the National Aeronautics and Space Administration (NASA) DC-8 and P3-B aircraft were made as part of the NASA/GTE PEM-Tropics B mission during the Spring of 1999. The target species were directly coupled to tropospheric oxidants as sources of odd-hydrogen and odd-oxygen radicals, as reservoirs of the same, and as conductors in their loss. The net production of ozone or odd-oxygen in the troposphere was largely predicted on the basis of photochemical point model simulations based upon measured concentrations of hydrocarbons, nitric oxide, water, carbon monoxide, ozone, and sunlight and both measured and model diagnosed concentrations of nitrogen dioxide, perhydroxyl, methylperoxyl, and hydroxyl radicals. The species measured provided mechanistic insight and chemical constraints to these purely chemical model simulations and provided an additional measure of confidence in their results. Multi-dimensional space-time models suggested that atmospheric motions, the vertical transport and mechanical redistribution of the hydroperoxides, may have a profound effect on odd-O and odd-H chemistry in the upper troposphere. The proposed hydrogen peroxide, methylhydroperoxide, and formaldehyde measurements gave needed information on transport, chemical redistribution, and scavenging by cloud and precipitation systems (meteorological conditions which have a larger role in the tropospheric chemistry than in PEM-Tropics A). Also, the target species were coupled to the gas-phase and, more significantly, to the heterogeneous chemistry of sulfur dioxide and its oxidation to sulfuric acid.

During the past year we completed several examinations of the data in relation to importance atmospheric chemical cycles resulting in several papers in press or in the publication process.

Gas Phase Measurements of Hydrogen Peroxide, Methylhydroperoxide, and Formaldehyde During TRACE-P

Researchers: Assistant Professor Daniel W. O'Sullivan, Co-PI
and Dr. Brian G. Heikes (PI; University of Rhode Island)
Sponsor: National Aeronautics and Space Administration (NASA)

We performed measurements of gas-phase hydrogen peroxide, methylhydroperoxide, and formaldehyde on board the NASA DC-8 aircraft as part of the NASA/GTE TRACE-P mission. The target species were directly coupled to tropospheric oxidants and ozone as sources of odd-hydrogen and odd-oxygen radicals, as reservoirs of the same, and as conductors in their

loss. The target species were coupled to the gas-phase and, more significantly, to the heterogeneous chemistry of sulfur dioxide and its oxidation to sulfuric acid. The species measured provided mechanistic insight and chemical constraints to chemical model simulations and provided an additional measure of confidence in their results. Multi-dimensional space-time models suggested that atmospheric motions, the vertical transport and mechanical redistribution of the hydroperoxides, may have a profound effect on odd-O and odd-H chemistry in the upper troposphere. The hydrogen peroxide, methylhydroperoxide, and formaldehyde measurements added information on transport, chemical redistribution, and scavenging by cloud and precipitation systems. The proposed HPLC hydroperoxide measurement system has been flown on both the DC-8 and P3B aircraft in several NASA field programs to date (PEM-Tropics A&B and on the DC-8 in PEM-West A&B, TRACE-A and SONEX), and recently on the NCAR C-130 during the NSF sponsored TOPSE experiment. It uniquely quantifies hydrogen peroxide, methylhydroperoxide, and other low carbon number organic hydroperoxides when present. Measurement time resolution, precision and estimated accuracy are within prescribed limits. The proposed formaldehyde instrumentation has been flown and achieved time resolution, precision, and estimated accuracy within prescribed limits in the NASA programs TRACE-A, SONEX and PEM Tropics B. This effort is tightly coupled to measurements of these same species made onboard the P3-B through pre- and post-mission instrument comparisons, standard exchange in the field at co-located sites and calibration and blank protocols. Preliminary measurements were submitted in the field, within 24 hours after local flights and within 48 hours of transit flights. Data is then resubmitted to the archive within 31 days of the instruments returning from the field, after post-mission calibrations of flow, temperature, and pressure sensors and stock standards are incorporated into data reduction algorithms. Final data will be submitted to the archive after the first data workshop. Post mission the gathered data will be analyzed in conjunction with the entire science team. Measurement distributions and correlations with other species measurements will be examined with respect to air mass characterization and cloud processing. Analysis and interpretation of our measurements with respect to tropospheric oxidants, net oxidant production, and sulfur gas oxidation will be performed collaboratively with other members of the science team using our own and more sophisticated meteorological transport and photochemical models. The role of hydroperoxides and formaldehyde in odd-H chemistry, net ozone production, and heterogeneous sulfur chemistry will be examined.

Dielectric and Mechanical Properties of Polydimethylsiloxane Networks

Researcher: Associate Professor Maria J. Schroeder
Sponsor: Naval Research Laboratory (NRL)

Silicones are utilized in a variety of applications ranging from elastomers to lubricating oils to adhesives. Characterizing the behavior of these materials can lead to improvements in their preparation and application. Model networks of polydimethylsiloxane (PDMS) have been synthesized with a broad range of structures by controlling crosslinking agent, catalyst, and curing conditions. Linear PDMS polymers ranging in molar mass from 186 to 28000 g/mol were used to create model PDMS networks of varying crosslink density and hence different levels of molecular constraint. A tetrafunctional crosslinker allows four PDMS chain attachments per crosslink and results in a well-defined network system. Thermal mechanical analysis indicates that the coefficient of thermal expansion and temperature of crystallization for the networks are correlated to crosslink density. However, the highest crosslink density samples did not exhibit crystallization even at slow cooling rates. Dielectric spectroscopy results suggest a broadening of the dispersion with crosslink density and a strong temperature dependence of the relaxation times. Mechanical tests further corroborate the relationship between physical properties and the molecular structure of the networks.

Conformational Analysis of Bioactive Compounds

Researcher: Associate Professor Joseph J. Urban
Sponsor: Naval Academy Research Council (NARC)

Acetylcholine is a major neurotransmitter in both the central and peripheral nervous systems. The cholinergic nerve transmission system is of particular importance to the military because this system is the target of the organophosphorous G nerve agents. The mechanism of action of these agents is to block nerve transmission by inhibition of the enzyme acetylcholinesterase, an essential component of the nerve transmission process. Upon binding to its receptor acetylcholine undergoes a conformational change and NMR studies that have been reported in the literature provide a hypothesized “bound conformation” (to the nicotinic acetylcholine receptor). The energy cost associated with this conformational change, however, is not known and is extremely difficult to estimate experimentally. In this work a combination of molecular modeling techniques have been

employed to determine the difference in energy between the bound and unbound conformations of acetylcholine. The results indicate that the bound conformation reported in the previous NMR work lies significantly above the ground state in energy. This suggests that further experimental work is needed to establish the bioactive conformation of acetylcholine when bound to its receptor. In addition, this work established the effects of substituents (N-methyls) and the surrounding environment on the conformational preferences of acetylcholine and similar systems.

Self-Assembly Approaches to Molecular Electronic Devices

Researcher: Assistant Professor Craig M. Whitaker
Sponsor: Naval Research Laboratory (NRL)

This project focuses on the design and requirements for molecular computer circuits that incorporate gain-producing elements. I am the team leader for the synthetic portion of the project through the Naval Research Laboratory that includes collaboration between many different institutions (Cornell University, Scripps University, the University of South Carolina, the University of North Texas and the MITRE Corporation). We are creating organic molecules based on a phenylacetylene architecture that can self-assemble on a highly symmetric virus. The virus nanoblocks can then be used to construct the elements required to produce the desired computer circuits.

Independent Research

Synthesis of New Polydentate Ligands

Researchers: Associate Professor Debra K. Dillner
and Associate Professor JudithAnn R. Hartman

The target molecules for this project were new podand ligands that can be prepared from tris(3-aminopropyl)amine. These compounds are designed to form stable complexes with transition metals. Previous studies in Prof. Hartman's laboratory examined similar podands prepared from tris(2-aminoethyl)amine. The compound prepared in this study incorporates an additional methylene group on each arm of the podand. This will affect its ability to ligate to transition metals of various ionic radii.

Preparation of the ligands first required preparation of the tris(3-aminopropyl)amine. This compound is not commercially available although it has been previously described in the literature. The first step in the synthesis is the Michael condensation of three equivalents of acrylonitrile with ammonia. Several literature methods for this step failed to produce the desired material. Finally, this condensation was carried out using an *in situ* two step procedure, resulting in approximately 80% yield of the desired tris(2-cyanoethyl)amine. Reduction methods for the subsequent step were then investigated and optimized. Of the variety of procedures tested, a room temperature, hydroxide mediated, hydrazine and Raney-nickel reduction was the most successful, resulting in a 60% yield for this step to produce the desired triamine. The tris(3-aminoethyl)amine then underwent reductive coupling with pyridine carboxaldehyde to produce the desired podand. The yield for the final step was quantitative and the overall yield for the sequence is 48% from inexpensive, readily available materials.

With the synthetic route now established, studies of the binding of the podand to transition metals will be studied in the Hartman laboratories. As alternate final couplings are needed, they will be carried out using the methodology described above.

Investigation of the Physical Properties of Carbon Nanotubes

Researchers: Dr. Carter T. White (NRL), Dr. Daniel H. Robertson (IUPUI)
and Associate Professor Judith A. Harrison

It has been recently proposed that carbon nanotubes might constitute well-defined tips for scanning probe microscopies (SPM). Multiwalled nanotubes have been shown to perform well as SPM tips when used in tapping mode, due to their desirable combination of stiffness and flexibility. We have been using molecular dynamics simulations to examine the physical properties

of hemispherically-capped carbon nanotubes. These simulations provided insight into the utility of these tubes as scanning force microscope tips. Simulations demonstrate that the capped nanotubes, although undergoing complex deformations, have the remarkable ability to recover reversibly when pushed into a hard substrate, such as diamond.

The lateral and transverse motions of [n,n] single-walled nanotubes have been investigated. These results show that single-walled nanotubes vibrate in both the transverse and the lateral directions. Examination of [10,10] nanotubes of various lengths revealed that the frequency of the vibrations was linear with the square of the nanotube length. The frequency of lateral vibrations of nanotubes with different radii was shown to be linear with radius. More recently, we have examined the usefulness of double-wall nanotubes as SPM tips compared to single-wall nanotubes. These results were presented at the 2000 Fall Meeting of the *Materials Research Society* in Boston.

Molecular Dynamics Simulations of the Bending of Filled Carbon Nanotubes

Researchers: Dr. Paul Mikulski (Post-Doctoral Fellow)
and Associate Professor Judith A. Harrison

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.

Online General Chemistry Laboratory Submissions: Assessment

Researchers: Associate Professor Joseph F. Lomax and
Capt Melonie Teichert, USAF (Assistant Professor at USNA)

The Midshipman Online Laboratory System (MOLS) is a web-based system that allows students to input their numerical data and analysis. To give the students direct and immediate feedback, an error flag visually indicates a calculation error. The instructors can use the input values to evaluate the student work providing a valuable tool to speed grading. The system has over 15 general chemistry labs and has been well received by the hundreds of students and two dozen faculty who have used it over the last three years. To improve the system, data was collected about how the students react to the program in general, and how the students use the error flags to troubleshoot their calculations. The data was collected using student surveys and focus groups. Preliminary web-based surveys have given us information on how to structure newer online surveys and how to develop questions for the focus groups. Summer school students will be used in the new surveys and focus groups. Permission from Institutional Research has been obtained and we hope to present our findings at the Fall American Chemical Society Meeting.

Online General Chemistry Laboratory Submissions: Advances

Researchers: Associate Professor Joseph F. Lomax and
Associate Professor Debra K. Dillner

The Midshipman Online Laboratory System (MOLS) is a web-based system that allows students to input their numerical data and analysis. To give the students direct and immediate feedback, an error flag visually indicates a calculation error. The instructors can use the input values to evaluate the student work providing a valuable tool to speed grading. The system has over 15 general chemistry labs and has been well received by the hundreds of students and two dozen faculty who have used it over the last three years. Additional laboratory experiments have been added to MOLS, including an electrochemistry lab and a kinetics lab. Improvements have been made in the structure of the programs. A more easily constructed method for assigning variables has sped development of new labs. This method also has made it possible to move to a relational database system. The system has been ported to a NT system. These improvements make it possible to utilize the Academy's Oracle Database system. Hopefully, during the summer intercessional, problems associated with the database interfacing will be overcome and we will be able to contract with Prentice Hall Publishers to publish MOLS in conjunction with their online laboratory system.

Intercalation Chemistry: An Undergraduate Inorganic Chemistry Laboratory

Researchers: Associate Professor Joseph F. Lomax and
Mr. Matthew Schroeder, Chemist, (USNA Chemistry Department)

An intercalation is a reaction where the basic structure of a solid is maintained during a chemical reaction. The swelling of clay with water and the reaction of lithium with titanium disulfide in the cathode a common type of battery are examples. However, this type of reaction is almost completely absent from the chemical education literature because 1) the most common analytical technique used is Powder X-Ray Diffraction (Powder XRD), 2) the original syntheses for these reaction involve high temperature (over 700°C) reactions, and 3) most involve non-stoichiometric compounds. Though uncommon at most undergraduate institutions, we are fortunate to have access to a Phillips Powder XRD diffractometer in the Physics Department. Recent developments in the field show that mild reducing agents such as sodium borohydride and potassium iodide are often sufficiently strong to effect intercalation at slightly elevated temperatures (<100°C). As to the non-stoichiometric compounds, students rarely become aware that one-phase non-stoichiometric solids can be formed and this lab gives them an opportunity to directly experience making and characterizing these compounds. In the SC410 Inorganic Chemistry Laboratory, five intercalation hosts, three intercalation ions and two stoichiometries were synthesized. This made for an exciting and research-like lab, but it also highlighted limitations in the synthesis and analysis. I intend to spend a significant part of the intercessional period refining and improving this student laboratory. I intend to present the student results and improvements at the Fall American Chemical Society Meeting and to test the improvements in SC410 Inorganic Chemistry Laboratory in the Spring.

Theoretical Calculations On $CoSO_2$

Researcher: Associate Professor Roy E. McClean

Semi-empirical, density functional theory, and RRKM calculations are currently being performed on the Co + SO_2 system. These calculations are being performed in support of the experimental investigation into the Co + SO_2 reaction. In that work, the $CoSO_2$ adduct is formed. The objective of this work is to determine the optimized geometries, vibrational frequencies, and energies of plausible isomers of $CoSO_2$.

PM3 calculations were performed using the Spartan suite of programs. It is a semi-empirical method that sometimes does an acceptable job in reproducing equilibrium geometries of substances containing transition metals. However, the parameters are not based on producing heats of formation. Higher-level calculations on other metal/SO_2 systems indicate that the side-on bonded, $\eta^2_{O,O}$ isomer (C_{2v} symmetry) is the most stable. Thus, the $\eta^2_{O,O}$ isomer of $CoSO_2$ was assumed (initially) to be the product of the Co + SO_2 reaction. Combining these results with the experimental results, and using them in RRKM calculations (a unimolecular rate theory) gave a binding energy of approximately 20 kcal mol^{-1}. Due to the nature of the PM3 method, this value and the equilibrium geometry are crude estimates. PM3 calculations are currently being performed on other isomers.

Higher level (and more expensive) calculations using density functional theory are also being performed on several isomers of $CoSO_2$. These calculations are accomplished through the Gaussian 98 suite of programs. Binding energies can be computed using density functional theory and compared to the binding energies from RRKM theory to determine the most likely reaction products.

Ozone And Carbon Monoxide Measurements At The Hendrix Laboratory Meteorological Station, United States Naval Academy

Researcher: Assistant Professor Daniel W. O'Sullivan

Assessment of air quality in Maryland is based upon the average hourly ozone concentration. The Maryland Department of the Environment (MDE) operates instrumentation and oversees the operation and data compilation from a network of air quality monitoring stations throughout Maryland. The monitoring stations perform measurements of ozone, O_3, at all locations and carbon monoxide, CO, nitrogen oxides, NO_x, and sulfur dioxide, SO_2 at selected locations. The daily air quality index for the Baltimore-Washington region is based solely on these ozone measurements.

Instrumentation was added to the Hendrix Oceanography Laboratory to monitor O_3 and CO at the Academy. Specifically, MDE transferred the instrumentation to the Naval Academy in the fall of 2000 and we began monitoring in November of 2000. I have assumed responsibility for the operation and calibration to meet the monitoring network requirements. Provided the measurements are successful and meet the quality control criteria, the data from the Naval Academy site would be incorporated into the Maryland monitoring network. In addition, USNA would have access to local, real-time air quality measurements for summer training decisions.

Photochemical Study of Cyano-Isocyanide-Phosphine Complexes of Iron and Ruthenium

Researcher: Professor Joyce E. Shade

The chemistry of carbonyl-cyano-phosphine complexes of iron has been studied extensively for the last ten years. In general, reflux or photolytic reaction conditions have been employed to initiate the loss of a carbonyl (CO) group from cyclopentadienyl-iron-carbonyl starting materials with a subsequent inclusion of a phosphine or phosphite ligand on the metal center. The resulting complexes obtained in these studies, however, all contain at least one carbonyl group. The purpose of this research was to prepare a series of anionic, neutral and cationic cyano, mono- and bisisocyanide complexes for reaction with phosphine or phosphite groups under photolytic conditions.

Photolysis of the monoisocyanide complex, $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(CNCH_3)$, in the presence of a slight excess of triphenylphosphine at room temperature gave the desired product $[(\eta^5\text{-}C_5H_5)Fe(CN)(CNCH_3(PPh_3)]$ with loss of one equivalent of carbon monoxide. Two additional products have been obtained, however: $(\eta^5\text{-}C_5H_5)Fe(CNCH_3)_2(CN)$ and $(\eta^5\text{-}C_5H_5)Fe(CN)(PPh_3)_2$. Similar results were obtained with a variety of phosphine, phosphite, arsine and antimony ligands. Several of the reaction products have been isolated from the fairly clean reaction mixtures and a variety of spectral data have been obtained to verify their identity. Further purification and characterization of these compounds is continuing. In addition, trends of reaction product yields with bulk and basicity of ligand are being studied. Effect of ligand identity (both on the metal prior to photolysis and as an incoming group), wavelength of the photolysis lamp and temperature of the reaction mixture are being studied as they affect the reaction products obtained. Anionic and cationic starting materials are being investigated under a variety of reaction conditions in order to analyze the system for any trend which might develop as a function of complex charge. A collaborative effort was established with Professor Antony Rest at The University in Southampton in an effort to conclusively identify the reaction intermediate(s). The results of this work have been very promising and the identity of the reaction intermediate has been postulated, as a result of low-temperature matrix isolation studies conducted by Prof. Rest. Work on the project is continuing with a shift in focus to the analogous ruthenium species. Manuscripts on the synthetic portions of the project as well as the spectroscopic matrix work are being prepared and final spectral data is being obtained for inclusion in the papers.

Enzymatic Repair Of Proteins Damaged By Oxidation

Researcher**:** Assistant Professor Virginia F. Smith

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 being investigated 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.

Control Of Intracellular Iron Regulation Of Iron Levels By Cytoplasmic Aconitase/IRP-1

Researcher**:** Assistant Professor Virginia F. Smith

Iron is crucial for a variety of physiological processes, however, it is present in very low abundance in the environment and is difficult for the cell to obtain. One way that nature has devised to ensure sufficient levels of iron is through the iron-responsive element protein-1 (IRP-1). The manner in which IRP-1 maintains intracellular iron levels is fascinating: When iron levels are low inside the cell, IRP-1 causes the levels of iron to rise by either increasing the production of proteins that bring in iron from outside or by causing iron-storage proteins to release the iron they were holding, making it available for other purposes. Once the iron concentration is restored to normal levels, IRP-1 becomes an iron-containing enzyme called aconitase that participates in energy production. In this project, protein folding techniques are being used to learn how IRP-1/aconitase can exist in two functionally distinct forms and how it is able to convert between these two forms reversibly and efficiently.

Research Course Projects

Synthesis and Study of Amine-Functionalized Silica Gels

Researchers: Midshipman 1/C Joshua D. Nassiri, USN
and Midshipman 1/C John M. Childs, USN
Adviser: Associate Professor JudithAnn R. Hartman

Doubly-templated silica gels were prepared in the presence of a sodium dodecyl sulfate surfactant and one of five metal ions, Cu(II), Zn(II), Mg(II), Mn(II), and Ni(II). Individual ion templates were not shown to increase specificity; rather, binding affinities for each metal ion did not change from substrate to substrate. The capacity, however, was shown to increase in relation to the number of ammine groups on the functionalized gel. Qualitatively, the tri-ammine functionalized gel had the highest capacity as expected, and the mono-ammine had the lowest capacity, also as expected. The quantitative relationship between ammine concentration and binding capacity was not linear, suggesting that some cooperative binding may have occurred.

Synthesis of Radiotracers for the Study of the Nicotinic Acetylcholine Receptor

Researcher: Midshipman 1/C Lucas S. McDonald, USN
Adviser: Associate Professor Christopher M. Kinter
Sponsors: Naval Academy Research Council (NARC) and the Division of Nuclear Medicine
and Radiation Health Sciences, The Johns Hopkins University

The endogenous cholinergic neurotransmitter, acetylcholine, exerts its biological effect via two types of cholinergic receptors: the muscarinic acetylcholine receptor (mAChRs) and the nicotinic acetylcholine receptors (nAChRs). Considerable effort has been directed at identification and characterization of ligands for nicotinic acetylcholine receptors. The interest in these compounds stems in part from evidence that agents acting at this receptor may have therapeutic utility in the treatment of a variety of central nervous system disorders including Alzheimer's and Parkinson's diseases, attention deficit or hyperactivity disorders, Tourette's syndrome and depression. Additionally, this receptor has been implicated in a variety of central processes such as learning, memory, and the relief of pain. Several potential compounds have been identified for use in the study of the nicotinic acetylcholine receptor and efforts have been directed towards their synthesis and radio-labeling with positron emitting isotopes

Water Soluble Mutagen Production During The Remediation Of Oil-Contaminated Soil

Researcher: Midshipman 1/C William C. Blodgett, Jr., USN
Advisers: Professor John Foerster (Oceanography Department)
Assistant Professor Daniel W. O'Sullivan
and Assistant Professor Virginia F. Smith (Chemistry Department)

The illegal disposal of used motor oil on land or in waterways creates problems for the environment and people, as well as fish and wildlife. Bioremediation is a natural process that uses microorganisms to transform harmful substances into non-toxic carbon dioxide, water and fatty acids. This purpose of this study was to determine if the bioremediation of naphthalene, a

common polycyclic aromatic hydrocarbon found in used motor oil, also produced water-soluble mutagens that could contaminate groundwater. It was hypothesized that mutageneic material produced would be the result of naphthalene's transformation into að-naphthol, a highly toxic hydrocarbon. A chemical assay, however, revealed that að-naphthol was not produced. An Ames assay (*Salmonella* mutagenicity test) was used to detect DNA frame-shift mutations that occurred during a three-week incubation of simulated groundwater inoculated with hydrocarbon-degrading bacteria. The Ames assay revealed the production of a lethal toxin during the second week of incubation, suggesting that the biodegradation of naphthalene produced a water-soluble, highly-toxic, mutagenic substance.

Investigation Of Amino Acid Analysis Methods

Researcher: Midshipman 1/C Jennifer M. Bombinski, USN
Adviser: Assistant Professor Virginia F. Smith

Determination of the amino acid composition of a protein or peptide is a fundamental and highly informative analytical process. The purpose of this project was to develop an amino acid hydrolysis and analysis method suitable for use by undergraduates at the Naval Academy in either a teaching or research lab situation. A gas phase acid hydrolysis method was adapted from published methods using equipment already in place. Two methods of amino acid analysis were investigated: a reversed phase high-pressure liquid chromatography (HPLC) method using fluorescence detection of derivatized amino acids and a gas chromatograph-mass spectroscopy (GC-MS) method, in which the amino acids were derivatized to become more volatile. The GC-MS method was found to be faster, more robust and easier to interpret than the HPLC method. Midshipman Bombinski wrote a detailed protocol for both amino acid hydrolysis and analysis that can be used by students or faculty members interested in performing this kind of analysis.

Stereocontrol in the Synthesis of Cyclopentanes

Researcher: Midshipman 2/C Jonathan D. McDivitt, USN
Adviser: Associate Professor Debra K. Dillner

Many terpene natural products contain cyclopentane rings with multiple stereocenters incorporated in that ring. Control of these stereocenters is difficult to achieve due to the inherent fluxional nature of the cyclopentane ring. In this investigation, the use of a rigid bicyclic template for introduction of stereocenters was studied.

Before the full study of stereocontrol in these systems can be undertaken, synthesis of the bicyclic template must be optimized. While the needed compound has been prepared previously in these laboratories, several of the synthetic steps were problematic. The first of steps to be optimized is the very first in the route. This involves a Diels-Alder reaction to form 4-carbomethoxy-1-cyclohexene. This can be produced from 1,3-butadiene and methyl acrylate. However, 1,3-butadiene is a hazardous gas and yields on this step were extremely variable. Use of butadienesulfone instead of 1,3-butadiene was attempted. After varying solvents, stoichiometries and temperatures, a satisfactory and reliable method for producing multigram quantities of the cyclohexene is now available.

Another difficult step in the route has been an oxidative cleavage of the double bond, combined with an *in situ* lactonization and esterification to form 3-(ethyl-3-propanoyl)-4,4-dimethylbutyrolactone. A literature search of oxidative cleavage methods led to five suitable methodologies. These were tried systematically. After this investigation, it was decided that the most cost-effective method of accomplishing this step was ozonolysis in formic acid, followed by addition of methanol and refluxing for two days.

With these improvements in the synthetic route to the bicyclo[3,3,0]octane template, studies on stereochemical control using this template can now be advanced.

Carbene Condensations With Diethyl Azodicarboxylate

Researchers: Midshipman 1/C Reed M. Heckert, USN
and Midshipman 1/C Andrew S. Waldmann, USN
Advisers: Associate Professor Debra K. Dillner, LCDR Paul Kaiser, USN
Sponsor: Albert G. Stern, Ph.D., NSWC, Indian Head Division

Highly energetic materials are of great interest to the Navy. Many of these materials are known and one factor in whether particular compounds find military application is cost of synthesis. The cost of a material is in turn determined by the difficulty of its synthesis. Difluoramines are very useful energetic materials but in some cases, the introduction of the 1,1-difluoroamine groups is problematic, requiring 3-4 synthetic steps. In this project, the feasibility of using a carbene addition route was undertaken.

It is known that difluoramines can be prepared from derivatives of diaziridines. Carbene addition of a suitable precursor with diethyl azodicarboxylate (DEAD) and its derivatives could lead to diaziridines. The chemical literature was searched for various methods of making carbenes. The carbenes needed to make energetic materials would be similar to dialkyl carbenes. There are only two generally applicable methods for making the appropriate dialkyl carbenes. These are from 1,1-dibromides and from diazirines. Preliminary investigations of both of these methods were undertaken.

The 1,1-dibromide compounds necessary are neither commercially available nor easily synthesized. The shortest synthetic route to 1,1-dibromocyclohexane found in the literature involved three synthetic steps, of which two give poor yields. While simple methylene carbene did add to diethyl azodicarboxylate, the overall prospect of replacing current methodologies with this type of carbene addition is not promising and no further studies are planned. While synthesis of the diazirine carbene precursor was much simpler, the carbene formation and condensation was problematic. This method may have promise using other reaction conditions or other synthetic steps to form the dicarboxy diaziridine derivatives.

Improved Optical Limiters

Researcher: Midshipman 2/C Peter D. Huffman, USN
Adviser: Professor Jeffrey P. Fitzgerald

Optical limiters are materials that are transparent to ambient, low-intensity light yet opaque to high-intensity light such as from lasers. Development of optical limiters is important to protect solder's and pilot's eyes and sensitive optical imaging devices from laser "dazzling."

The overall goal of this project was to design and synthesize better optical limiting materials. The project had two approaches. The first was basic research into the potential of the thallium ion to increase the optical limiting properties of the phthalocyanine molecule. Because of its proximity to lead and indium, which are among the based phthalocyanine-based optical limiters known, thallium phthalocyanine was prepared and studied.

The second approach to better optical limiting materials was the synthesis of a "clamshell" dimmer which would enforce dimerization of the phthalocyanine molecules. This was the first test of active aggregation control on the optical limiting properties of phthatlocyanines. If successful, this strategy can be extended to higher order aggregates.

Results so far include the synthesis of two different "clamshell" phthalocyanines. These need to be metallated with lead and then the optical limiting properties must be tested.

Synthesis and Characterization of Photoactive Antenna-Acceptor Molecules and Their Supramolecular Complexes with Helical Amylose

Researcher: Midshipman 1/C John E. Laird, USN
Adviser: Associate Professor William B. Heuer

Transition metal coordination complexes exhibiting strong metal-to-ligand charge-transfer (MLCT) transitions in the visible region have important applications as "antenna" groups in photochemical energy conversion systems. The tris-bipyridine ruthenium(II) ion ($Ru(bipy)_3^{2+}$) has been particularly well-studied in this regard, since visible excitation of this complex produces a long-lived triplet excited state, which is luminescent in fluid solution at room temperature. The excited triplet state is also a strong electron donor, and thus has been widely used in fundamental studies of photoinduced electron transfer reactions. For example, when an acceptor group, such as 4,4'-bipyridinium dication ("viologen"), is covalently attached via a saturated hydrocarbon bridge to the $Ru(bipy)_3^{2+}$ cation, visible excitation leads to electron transfer from the "antenna" complex to the viologen, a process which mimics the first step in photosynthesis. The lifetime of the charge-separated state arising from this transfer is largely determined by the rate of back electron transfer from the reduced viologen back to the oxidized Ru(III) complex, which is in turn governed by the proximity of the two groups. In an effort to increase this lifetime, we are investigating the use of supramolecular complexation by amylose as a means of enforcing spatial separation of the $Ru(bipy)_3^{2+}$ donor and viologen acceptor groups. In polar media, amylose (a linear polysaccharide) adopts a helical conformation with a hydrophobic cavity that is able to form inclusions with linear guest species. In order to encourage formation of the supramolecular complexes, we have attached long hydrocarbon tails (C_nH_{2n+1}, where n = 8 to 22) to the viologen group. Studies of the steady state emission of these complexes in DMSO/H_2O solutions, both in the presence and absence of amylose, indicate that for n = 16 or longer, inclusion does in fact occur, as indicated by modest increase in the luminescent emission of the antenna complex. Time-resolved flash-photolysis experiments will be conducted by a collaborating group at Bowling Green State University in order to determine the effect of amylose complexation upon the lifetime of the charge-separated state. Electrochemical studies of these complexes in the presence and absence of amylose are also planned, since it is anticipated that formation of the supramolecular complex should exert a strong influence on the reduction potential of the viologen acceptor.

Structural and Electronic Studies of Crystals Using X-ray Diffraction

Researcher: Midshipman 1/C R. J. Wheat, USN
Adviser: Associate Professor Wayne H. Pearson
Sponsor: Kinnear Research Fellowship

Work in the X-ray facility has involved investigations of the structural and electronic properties of materials. Structural studies involve the characterization of five different compounds containing combinations of either nickel or copper divalent metals with a series of aminopyridine compounds of varying coordination number. The coordination spheres are precipitated as either perchlorate or tetrafluorborate salts. Despite disordering in the anions, particularly the tetrafluorborates, the coordination spheres are well characterized. The purpose of this study is to compare the solid state structures with gas phase determinations of the coordination number. This work is in collaboration with Associate Professor Judith Hartman.Electronic studies of the para and meta substituted nitrobenzenes has continued through funding by a Kinnear Research Fellowship grant. Numerous attempts have been made to develop modeling procedures that would reveal pi bonding between the nitro group in substituted nitrobenzenes. Accurate, low-temperature X-ray data has been examined for these effects. Standard X-X high order refinements and charge analysis have led to results that could be explained using sigma inductive arguments as well as pi bonding. These analyses are based upon spherical modeling procedures and may fail for that reason. The next step in this work is to apply multipole refinement techniques to these compounds to not just reveal the aspherical component of the electron density but to directly model such density.

Synthesis of Mesogenic Terphenyl Derivatives (SC495)

Researcher: Midshipman 2/C J.C. Mitock, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsors: Naval Research Laboratory (NRL) and Office of Naval Research (ONR)

This project focused on the development of a synthesis of terphenyl derivatives that have different lateral substitutents and end-groups. In recent years, the synthesis of new mesogenic materials has increased dramatically in an attempt to satisfy the growing range of industrial applications. Much interest surrounds the family terphenyl compounds due to their ability to form interesting mesophases. These materials may also find widespread applications as host materials for display devices, in nonlinear optics, information storage, and twisted nematic electro-optic systems. We wanted to study how the addition of various substitutents affect the liquid crystalline properties of these terphenyl compounds. Hexyl terphenyl ether was synthesized to serve as the base molecule for further mesogenic studies.

Synthesis of Novel Nitric Oxide (NO) Releasing Compounds (SC496)

Researcher: Midshipman 2/C J.C. Mitock, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsor: Dr. John Toscano, The Johns Hopkins University

This research project focused on the development of a novel photochemical precursor for the delivery of nitric oxide (NO). Nitric oxide is an important bio-regulator that can act as a signal molecule to the nervous system, as a weapon against infection, and a regulator of blood pressure and blood flow. Johns Hopkins University provided the diazenium salt that is coupled with the compounds synthesized at the Academy. The DEA/NO compounds upon photolysis at 254 nm will release nitric oxide (NO).

Synthesis of New, Rigid-Rod Liquid Crystalline Materials (SC495)

Researcher: Midshipman 2/C David T. Russell, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsors: Naval Research Laboratory (NRL) and Office of Naval Research (ONR)

In recent years, the synthesis of new mesogenic materials has increased dramatically in an attempt to satisfy the growing range of applications. Mr. Russell's attempted to synthesize several homologues of dialkylterphenyls (**1**) then evaluate their mesogenic properties. Palladium-catalyzed cross-coupling reactions and Friedel-Crafts acylations were used in the synthesis of the novel compounds. These materials were prepared in order to understand the steric effects of lateral alkyl-substituents on mesomorphic properties. The mesomorphic behavior and hence the suitability for applications of compounds has been shown to depend strongly on the relative positions and types of the lateral substitutents incorporated into the materials. However, the chemistry involving the addition of the lateral side-chains has proven to be extremely difficult.

Self-Assembly Approaches to Molecular Electronic Devices (SC496)

Researcher: Midshipman 2/C David T. Russell, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsors: Office of Naval Research (ONR) and Naval Research Laboratory (NRL)

The main goal of this project was to demonstrate the feasibility of functional molecular electronic devices by using different types of self-assembly approaches. Our first task involved the optimization of the functionality of different classes of molecules that constitute the circuit elements of a molecular electronic device – switches, rectifying diodes, conductors and resistors. The studies initially looked at the synthesis and development of a molecular switch that posses a connection point (alligator clip) at both ends of the molecule for gold and palladium surfaces. We also designed and synthesized novel core structures for the optimization of the negative differential response (NDR) in the molecular wires.

Trident Scholar Project

Radiation-Induced Processing of Hydrocarbons in Environments Relevant to Pluto

Researcher: Midshipman 1/C Robert M. Gallagher, USN
Adviser: Professor Robert F. Ferrante
Sponsors: NASA/Goddard Space Flight Center
and U.S. Naval Academy Trident Scholar Program

An understanding of the formation of larger molecules in the outer solar system, by radiation induced processing of more primitive constituents, has implications relating to the evolution of the solar system. Organic residues formed by cosmic ray irradiation on cosmic ices may also have some exobiological significance, directly relating to the process from which life began on Earth. Since Pluto is one of the most primitive, and well-preserved, bodies in the solar system, its surface chemistry is of particular relevance. This project was an attempt to correlate recent astronomical data with a radiation model for compound formation.

Spectroscopic observations of Pluto suggest the presence of ethane, presumably caused by cosmic ray irradiation of methane trapped in solid nitrogen at the surface. This project used near-infrared (NIR) spectroscopy to examine this process in laboratory analogs. Samples of nitrogen doped to appropriate low concentrations with methane and/or carbon monoxide were deposited at 50 K or below, and the resulting films irradiated with varied doses of 1 MeV protons. The formation of ethane, and other products, was observed at radiation dosages consistent with levels experienced at the planet's surface. However, neither the intensity nor bandwidths of the spectroscopic signals compared very well with the NIR telescope data. These facts lend some support to a model suggesting two different terrains on the planet, one with low methane concentration, and another with much higher levels. Irradiation of the latter might account for ethane signals observable from earth. The laboratory irradiation experiments also resulted in the formation of a residue, stable at high temperatures, consistent with models of organic polymer formation on icy bodies in the outer solar system. Some attempts at determining the composition of the residue were also performed.

This project is near completion of the original objectives. We anticipate that results will be submitted for publication in the summer or fall of 2001.

Publications

Journal (Refereed) Manuscripts

Bitterwolf, T.E., Saygh, A. A., SHADE, J. E., Professor, Rheingold, A. L., Yap, G. P. A., and Liable-Sands, L., "Synthesis and Photochemistry of Ring-Coupled Heterobimetallic Compounds of Ruthenium. The Molecular Structures of $RuM(CO)_5(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4CR_2C_5H_4)$, where M = Mo, R = CH_3; M = W, R = H, $[Ru(CO)_2][Mo(CO)_3Cl](\mu\text{-}\eta^5, \eta^1\text{:}\ \eta^5\text{-}C_5H_4CH_2C_5H_3)$ and $[W(CO)_3][Ru(CO)_2Cl](\mu\text{-}\eta^5, \eta^1\text{:}\ \eta^5\text{-}C_5H_4CH_2C_5H_3)$," *Inorganic Chimica Acta*, 2000, Vol 300, pp. 800-809. (Invited paper.)

Reaction of the versatile reagent $Ru(CO)_2(\mu\text{-}\eta^5, \eta^1\text{-}C_5H_4CR_2C_5H_4)$, where R=H or CH_3, with $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$, where M=Mo or W, yields bimetallic compounds of the form $RuM(CO)_5(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4CR_2C_5H_4)$ in excellent yield, while reaction with $Fe(CO)_5$ yields $RuFe(CO)_2(\mu\text{-}CO)_2[\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ in excellent yield. Reaction with $Ni(CO)_4$ yields thermally unstable $RuNi(CO)_3[\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$. These compounds have been characterized by IR and NMR spectroscopies, and, with the exception of the Ru/Ni compound, elemental analysis. Photolysis of $RuMo(CO)_5[(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ in the presence of triphenylphosphine yields both of the simple mono-carbonyl substitution products with the phosphine on Ru and Mo. Photolysis of the derivative with phosphine bound to the molybdenum yields $[Ru(\tilde{A}\text{-}C_6H_5)(CO)][Mo(CO)_2][\mu\text{-}P(C_6H_5)_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4)$[Ru-Mo]. Photolysis of $RuFe(CO)_2(\mu\text{-}CO)_2[\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ with triphenylphosphineyields $[Ru(CO)]\{Fe[P(C_6H_5)_3]\}(\mu\text{-}CO)_2[\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$[Ru-Fe]. Photolysis of the Ru/Mo and Ru/W heterobimetallic compounds in deuterobenzene established that two metal-hydride species were formed, one whose chemical shift was characteristic of a $CpRu(CO)_2H$ and the second typical of a $CpM(CO)_3H$.

Photolysis of the Ru/Mo and Ru/W compounds in 20% chloroform in benzene followed by chromatography of the reaction mixtures permitted isolation of the isomeric photoproducts as their chloride derivatives. IR and NMR spectroscopy and X-ray crystallography of these compounds established them to have 'twist' structures in which one cyclopentadienyl ring is ·[1] to one of the metals and η^5 to the second. The molecular structures of four compounds were determined: $RuMo(CO)_5[(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$: monoclinic, $P2_1/n$, $a = 9.608(3)$, $b = 12.613(4)$, $c = 14.467(5)$ Å, ² = 97.59(2)°, $V = 1738.0(9)$ Å^3, $z = 4$, $R_F = 3.53$. $RuW(CO)_5(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4CH_2C_5H_4)$: monoclinic, $P2_1/c$, $a = 14.232(5)$, $b = 7.833(3)$, $c = 13.771(5)$ Å, ² = 93.22(3)°, $V = 1533(1)$ Å^3, $z = 4$, $R_F = 3.88$. $[Mo(CO)_3][Ru(CO)_2Cl](\mu\text{-}\eta^5, \eta^1\text{: }\eta^5\text{-}C_5H_4CH_2C_5H_3)$: monoclinic, $P2_1/c$, $a = 10.259(9)$, $b = 12.666(5)$, $c = 13.451(5(5)$ Å, ² = 109.85(4)°, $V = 1641(1)$ Å^3, $z = 4$, $R_F = 2.72$. $[Ru(CO)_2][W(CO)_3Cl](\mu\text{-}\eta^5, \eta^1\text{: }\eta^5\text{-}C_5H_4CH_2C_5H_3)$: monoclinic, $P2_1/c$, $a = 12.793(3)$, $b = 9.485(2)$, $c = 13.450(2)$ Å, $b =$ 94.56(1)°, $V = 1626.8(6)$ Å^3, $z = 4$, $R_F = 3.67$.

Bitterwolf, T.E., Linehan, J.C., and SHADE, J.E., Professor, "Dihydrogen as a Reactant in the Photochemistry of Bimetallic Cyclopentadienyl Carbonyl Compounds," *Organometallics*, 2000, 19, pp. 4915-4917.

Dihydrogen has been found to react photochemically with bimetallic compounds of the form $[(\eta^5\text{-}C_5H_5)M(CO)_n]_2$, where M = Mo or W, n = 3, M = Fe or Ru, n = 2, to give the corresponding metal hydrides, $(\eta^5\text{-}C_5H_5)M(CO)_nH$. Hydride formation is only significant when the photolysis wavelengths are in the high-energy regions known to trigger CO loss from these compounds, and hydride formation is suppressed by added CO, making it likely that the reaction involves oxidative addition of H_2 to an electron-deficient, CO-loss intermediate.

Bitterwolf, T. E., Linehan, J.C., and SHADE, J.E., Professor, "Solution and Nujol Matrix Photochemistry of $(\eta^5\text{-}C_5H_5)_2Os_2(CO)_4$ and Nujol Matrix Photochemistry of $(\eta^5\text{-}C_5H_4CH_3)_2Ru_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)M(CO)_2H$, where M = Ru and Os," *Organometallics*, 2001, 20, pp. 775 – 781.

Lowering the temperature of a Nujol solution of $(\eta^5\text{-}C_5H_4CH_3)_2Ru_2(CO)_4$ containing bands of the *trans*- and *cis*-bridging and *trans*-nonbridging isomers from room temperature to ca. 90 K results in complete disappearance of the bands of the *trans*-terminal isomer. The photochemistry of $(\eta^5\text{-}C_5H_4CH_3)_2Ru_2(CO)_4$ in frozen Nujol at 90 K differs subtly from that of $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ in inert gas matrixes at 12 K in that the *trans*-bridging isomer is found to undergo photolysis at high energy ($»_{irr}$ > 250 nm) to yield both the triply bridged carbonyl-loss species, $(\eta^5\text{-}C_5H_4CH_3)_2Ru_2(\mu\text{-}CO)_3$, and the *cis*-bridged species isomer. There is no evidence for formation of the *trans*-nonbridged isomer upon photolysis as observed for $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$. The solution photochemistry of $(\eta^5\text{-}C_5H_5)_2Os_2(CO)_4$ is shown to closely parallel that of $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$. Photolysis of $(\eta^5\text{-}C_5H_5)_2Os_2(CO)_4$ in $CHCl_3$ yields $(\eta^5\text{-}C_5H_5)Os(CO)_2Cl$, while photolysis in benzene yields hydride products believed to arise from metal-to-metal coupling of radicals. Photolysis of $(\eta^5\text{-}C_5H_5)_2Os_2(CO)_4$, which exists only in a nonbridged form, in frozen Nujol (90 K) results in CO loss and formation of $(\eta^5\text{-}C_5H_5)_2Os_2(\mu\text{-}CO)_3$ as the only photoproduct. Photolysis of $(\eta^5\text{-}C_5H_5)M(CO)_2H$, where M = Ru or Os, in frozen Nujol yields $(\eta^5\text{-}C_5H_5)M(CO)H$ and a second product that appears to be either $(\eta^5\text{-}C_5H_6)M(CO)_2$ or the $(\eta^5\text{-}C_5H_5)M(CO)_2$ radical.

CAMPBELL, M.L., Associate Professor, "Kinetic Study of Gas Phase $Lu(a^2D_{3/2})$ with O_2, N_2O and CO_2," *Chemical Physics Letters*, 330 (2000), pp.547-550.

The second-order rate constants of gas-phase $Lu(^2D_{3/2})$ with O_2, N_2O and CO_2 from 348 to 573 K are reported. In all cases, the reactions are relatively fast with small barriers. The disappearance rates are independent of total pressure indicating bimolecular abstraction processes. The bimolecular rate constants (in molecule^{-1}cm^{3}s^{-1}) are described in Arrhenius form by $k(O_2) = (2.3\pm0.4)x10^{-10}exp(-3.1\pm0.7$ kJ mol^{-1}/RT), $k(N_2O) = (2.2\pm0.4)x10^{-10}exp(-7.1\pm0.8$ kJ mol^{-1}/RT), $k(CO_2) = (2.0\pm0.6)x10^{-10}exp(-7.6\pm1.3$ kJ mol^{-1} /RT), where the uncertainties are $\pm2\sigma$.

CAMPBELL, M.L., Associate Professor, co-author, "Kinetic Study of the Reactions of Gas Phase $V(a^4F_{3/2})$, $Cr(a^7S_3)$, $Co(a^4F_{9/2})$, $Ni(a^3F_4, a^3D_3)$ and $Zn(4s^2\ ^1S_0)$ with Nitrous Oxide," *Journal of Physical Chemistry A*, 104 (2000), pp.11147-11153.

The reactivity of gas phase $V(a^4F_{3/2})$, $Cr(a^7S_3)$, $Co(a^4F_{9/2})$, $Ni(a^3F_4, a^3D_3)$ and $Zn(4s^2\ ^1S_0)$ with N_2O as a function of temperature and pressure is reported. The transition metal atoms were produced by the photodissociation of an

appropriate precursor molecule and detected by laser-induced fluorescence. The vanadium, chromium and cobalt rate constants are independent of total pressure indicating bimolecular abstraction reactions. The bimolecular rate constants are described in Arrhenius form by: $k[V(a^4F_{3/2})] = (4.7 \pm 0.7) \times 10^{-11}\exp(-10.8 \pm 0.5\ kJ\cdot mol^{-1}/RT)$, $Cr(a^7S_3)$, $(5.0 \pm 1.0) \times 10^{-11}\exp(-21.1 \pm 0.7\ kJ\cdot mol^{-1}/RT)$ and $Co(a^4F_{9/2})$, $(1.9 \pm 0.3) \times 10^{-10}\exp(-48.8 \pm 0.8\ kJ\cdot mol^{-1}/RT)$ where the uncertainties represent ± 2Fð. The reactions of nickel with N_2O are pressure dependent indicating adduct formation; however, the reaction also has a bimolecular component. The room temperature limiting low-pressure third-order and limiting high-pressure second-order rate constants are $(8.2 \pm 2.4) \times 10^{-32}$ molecule^{-2}cm^{6}s^{-1} and $(1.3 \pm 1.2) \times 10^{-12}$ molecule^{-1}cm^{3}s^{-1} in N_2 buffer, respectively. The second-order rate constant for the abstraction channel for the reaction of nickel with N_2O at 298 K is $(9.3 \pm 1.3) \times 10^{-14}$ molecule^{-1}cm^{3}s^{-1}. The reaction of zinc with N_2O is very slow; at 623 K an upper limit of 1×10^{-16} molecule^{-1}cm^{3}s^{-1} is set for this reaction. An assessment of the semi-empirical configuration interaction model used by Fontijn and co-workers to estimate barrier heights in these reactions is made.

CAMPBELL, M.L., Associate Professor, co-author, "Kinetic Study of the Gas Phase Reaction of $Ca(^1S_0)$ with O_2 from 296 – 623 K," *Journal of Physical Chemistry A*, 105 (2001), pp.3515-3520.

The reactivity of gas-phase ground-state calcium atoms with O_2 is reported from 296 to 623 K. Calcium atoms were produced by the photodissociation of $Ca(FOD)_2$ [where FOD represents the 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate ion] and detected by laser-induced fluorescence. Calcium recombines with O_2 to form CaO_2 in a reaction that exhibits a positive temperature dependence and is significantly in the fall-off region even at pressures as low as 10 torr. *Ab initio* quantum calculations are used to show that the reaction most likely proceeds on a triplet surface, where the Ca atom inserts into the O-O bond to form a triplet dioxide ($^3B_2$) with a very low frequency bending mode. The surprisingly large rate coefficient at elevated temperatures is explained by the correspondingly high density of rovibrational states, and the positive temperature dependence by a small barrier in the entrance channel at the crossing point between the covalent and ionic diabats. RRKM theory, fitted to the experimental data, predicts the following expression for the rate coefficient from 140 to 1000 K and 10^{-5} to 10^3 torr: $\log_{10}(k_{rec,0}/\ cm^6\ molecule^{-2}\ s^{-1}) = -57.10 + 19.70 \log_{10}T - 3.410 (\log_{10} T)^2$, $k_{rec,¥} = 1.36 \times 10^{-10} \exp(-1020/T)$ cm^3 molecule^{-1} s^{-1}, and $F_c = 0.67$.

COPPER, C.L., Associate Professor and KOUBEK, E., Professor, "Analysis of an Oxygen Bleach: A Redox Titration Lab," *Journal of Chemical Education*, 78 (2001), p.652.

An experiment is presented which allows students to balance an oxidation-reduction reaction equation and use the reaction to analyze a consumer product. Specifically, the experiment calls for students to balance the reaction of H_2O_2 and MnO_4^- two different ways (one assuming that H_2O_2 is the oxygen source and a second assuming that MnO_4^- is the oxygen source). The students then determine which of these balanced equations has the correct stoichiometry by titrating a standard H_2O_2 solution with $KMnO_4$. Finally, they use the correct balanced equation to determine the mass percent of H_2O_2 in commercially available, "environmentally friendly" oxygen bleach solution.

De LONG H.C., Major, (USAF) and Assistant Professor, co-author, "Physical and Electrochemical Properties of Substituted Imidazolium Based Ionic Liquids in both the Pure and Lithiated Form," *Progress in Molten Salt Chemistry 1*, R. F. Berg and H. A. Hjuler, Eds., Elsevier, New York, 511–522 (2000).

The physical and electrochemical properties of the molten salts 1-ethyl-3-methyl imidazolium tetrafluoroborate ($EMIBF_4$), 1,2-dimethyl-3-n-propyl imidazolium tetrafluoroborate ($DMPIBF_4$), and the new molten salts 1,2-dimethyl-3-n-butyl-imidazolium tetrafluoroborate ($DMBIBF_4$) and 1,2-dimethyl-3-n-butyl-imidazolium hexafluorophosphate ($DMBIPF_6$) characterized by temperature dependent ionic conductivity measurements and electrochemical intercalation studies on both the pure molten salt and with 0.5 M Li^+ present. Conductivity measurements indicate that the ionic conductivities of the molten salts at room temperature were 11.55 mS/cm, 5.67 mS/cm, 0.23 mS/cm, and 0.77 mS/cm, for $EMIBF_4$, $DMPIBF_4$, $DMBIBF_4$, and $DMBIPF_6$, respectively. Addition of 0.5 M Li^+ to the molten salts resulted in a decrease in their room temperature ionic conductivities, most likely due to their increased viscosity. For both the lithiated and pure molten salts, Arrhenius behavior was

observed for the temperature dependent ionic conductivity data, allowing for a straightforward determination of their respective E_a's.

HARRISON, J.A., Associate Professor, "Periodicities in the Properties Associated with the Friction of Model Self-Assembled Monolayers," *Tribology Letters*, 10 (2001) pp. 29-38.

The classical molecular dynamics simulations presented here examine the periodicities associated with the sliding of a diamond counterface across a monolayer of hydrocarbon chains that are covalently bound to a diamond substrate. Periodicities observed in a number of system quantities are a result of the tight packing of the monolayer and the commensurate structure of the diamond counterface. The packing and commensurability of the system force synchronized motion of the chains during sliding contact. This implies that the size of the simulations for the special case can be reduced so that the simulations can be conducted with sliding speeds and time durations that may bridge the gap between theory and experiment.

HARTMAN, J.R., Associate Professor, "An In-Class Experiment to Illustrate the Importance of Sampling Techniques and Statistical Analysis of Data to Quantitative Analysis Students," *Journal of Chemical Education*, 2000, 77(8), pp.1017-1018.

A simple in-class experiment designed to show the importance of sampling protocol and the use of statistics in data analyses is described. Two samples are presented to the class, an unmixed core sample and a mixed core sample. Both samples contain equal amounts of two colors of otherwise identical candies. The candies in the unmixed sample are in two separate layers in a tall opaque cup and the candies in the mixed sample are in a paper bag. The class is divided into two groups, each of which repeatedly analyzes one of the samples by each person drawing out one candy. The results from each analysis (as a percentage of one of the colors) is tabulated on the blackboard. These results are used to discuss what constitutes a good sampling protocol and a good sample. In addition, these results are used throughout the entire unit on statistics to demonstrate many calculations such as pooling data, comparison of means, confidence limits, and the use of Student's t-tests. This demonstration has proved to be useful for engaging the interest of most students in sampling and statistics, and is a particularly effective means of teaching active learners the very formalistic subject of statistics.

McCLEAN, R.E., Associate Professor, "Depletion Kinetics of Chromium Atoms by Sulfur Dioxide," *Journal of Physical Chemistry A*, 104 (2000) p.8723.

The gas phase depletion kinetics of Cr(a^7S_3, a^5S_2, a^5D_J) in the presence of SO_2 are reported. Chromium atoms were produced by the 248 nm photodissociation of chromium carbonyl and were detected by laser-induced fluorescence. The ground state of Cr, a^7S_3, was found to react rapidly via a termolecular mechanism with SO_2. At 297 K, the limiting low-pressure third order rate constant is $k_o = (2.68 \pm 0.41) \times 10^{-28}$ cm^6 molecule^{-2} s^{-1}, and the limiting high-pressure second order rate constant is $k_{hp} = (2.73 \pm 0.38) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; the uncertainties represent $\pm 1\sigma$ in precision. k_o was found to decrease with increasing temperature. The binding energy of $CrSO_2$ is estimated at 53 kcal mol^{-1} from combining the kinetic results with unimolecular rate theory and density functional theory. Cr(a^5S_2) depleted with a rate constant of $k = 6.32 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and the a^5D_J spin/orbit states depleted at the collision rate of 2.97×10^{-10} cm^3 molecule^{-1} s^{-1}; overall uncertainties are estimated at $<35\%$. Both chemical and physical quenching are likely for the excited states. The present work completes a study on the depletion kinetics of group 6 transition metal atoms by SO_2. Results are interpreted in terms of long-range attractive forces between Cr and SO_2 and the orbital occupancies of Cr atomic states.

O'SULLIVAN, D. W., Assistant Professor, co-author, "An Assessment of HO_x Chemistry in the Tropical Pacific Boundary-Layer - Comparison of Model Simulations with Observations Recorded During PEM Tropics-A," *Journal of Atmospheric Chemistry*, 38(3), (2001), pp.317-344.

Reported are the results from a comparison of OH, H_2O_2, CH_3OOH, and O_3 observations with model predictions based on current HO_x-CH_4 reaction mechanisms. The field observations are those recorded during the NASA GTE field program, PEM-Tropics A. The major focus of this paper is on those data generated on the NASA P-3B

aircraft during a mission flown in the marine boundary layer (MBL) near Christmas Island, a site located in the central equatorial Pacific (i.e., 2 degrees N, 157 degrees W). Taking advantage of the stability of the southeastern trade-winds, an air parcel was sampled in a Lagrangian mode over a significant fraction of a solar day. Analyses of these data revealed excellent agreement between model simulated and observed OH. In addition, the model simulations reproduced the major features in the observed diurnal profiles of H_2O_2 and CH_3OOH. In the case of O_3, the model captured the key observational feature, which involved an early morning maximum. An examination of the MBL HO_x budget indicated that the O(D-1) + H_2O reaction is the major source of HO_x while the major sinks involve both physical and chemical processes involving the peroxide species, H_2O_2 and CH_3OOH. Overall, the generally good agreement between model and observations suggests that our current understanding of HO_x-CH_4 chemistry in the tropical MBL is quite good; however, there remains a need to critically examine this chemistry when both CH_2O and HO_2 are added to the species measured.

SMITH, V.F., Assistant Professor, co-author, "Testing the Role of Chain Connectivity on the Stability and Structure of Dihydrofolate Reductase from E.coli: Fragment Complementation and Circular Permutation Reveal Stable, Alternatively Folded Forms," *Protein Science*, 2000, *10*, p.116.

The effects of chain cleavage and circular permutation on the structure, stability and activity of dihydrofolate reductase (DHFR) from *Escherichia coli* were investigated by various spectroscopic and biochemical methods. Cleavage of the backbone after position 86 resulted in two fragments, {1-86} and {87-159}, each of which are poorly structured and enzymatically inactive. When combined in a 1:1 molar ration, however, the fragments formed a high affinity complex that displays a weakly cooperative urea-induced unfolding transition at micromolar concentrations and retains about 15% of the enzymatic activity of full-length DHFR. A circularly permuted form with its N-terminus at position 86 has similar overall stability and secondary structure compared to full-length DHFR, but has reduced activity (~50%), altered side-chain packing and contains an equilibrium intermediate. These results highlight the importance of protein-ligand interactions in stabilizing the active-site architecture of DHFR.

Vachet, R.W., HARTMAN, J.R, Assistant Professor, Gertner, J.W., and Callahan, J.H., "Elucidation of Metal Complex Coordination Structure Using Collision-Induced Dissociation and Ion-Molecule Reactions in a Quadrupole Ion Trap Mass Spectrometer," *Int. J. of Mass. Spec*, accepted and in press.

Ion-molecule (I-M) reactions have been combined with collision-induced dissociation (CID) in a quadrupole ion mass spectrometer to provide the coordination structure of a series of first-row transition metal complexes. The metal complexes are generated by electrospray ionization, and the coordination number of these metal complex ions are determined in the gas phase using I-M reactions. The coordination sphere structure is then determined by dissociating the metal complexes, reacting their product ions, and comparing the coordination number of the product ions with their parent ions. Results show that a change in the coordination number upon dissociation identifies functionality involved in coordination to the metal. Conversely, no change in the coordination number indicates loss of a functional group that is not involved in the coordination to the metal. It was also observed that some product ions did not provide any useful coordination information upon reaction. In these cases, the product ions either did not contain the metal or contained the metal in a reduced oxidation state. The rearrangement of ligands upon dissociation to fill vacant coordination sites was expected to add significant ambiguity to the coordination determination, but in the limited cases studied here this occurrence was not seen.

Conference Proceedings

CAMPBELL, M.L., Associate Professor, "Kinetic Study of the Gas Phase Reaction of $Ca(^1S_0)$ with O_2 from 296 – 623 K," *16th International Symposium on Gas Kinetics*, Cambridge, England, 23 July 2000.

The reactivity of gas-phase ground-state calcium atoms with O_2 is reported from 296 to 623 K. Calcium atoms were produced by the photodissociation of $Ca(FOD)_2$ [where FOD represents the 6,6,7,7,8,8,8-heptafluoro-2,2-

dimethyl-3,5-octanedionate ion]and detected by laser-induced fluorescence. Calcium recombines with O_2 to form CaO_2 in a reaction that exhibits a positive temperature dependence and is significantly in the fall-off region even at pressures as low as 10 torr. *Ab initio* quantum calculations are used to show that the reaction most likely proceeds on a triplet surface, where the Ca atom inserts into the O-O bond to form a triplet dioxide ($^3B_2$) with a very low frequency bending mode. The surprisingly large rate coefficient at elevated temperatures is explained by the correspondingly high density of rovibrational states, and the positive temperature dependence by a small barrier in the entrance channel at the crossing point between the covalent and ionic diabats. RRKM theory, fitted to the experimental data, predicts the following expression for the rate coefficient from 140 to 1000 K and 10^{-5} to 10^3 torr: $\log_{10}(k_{rec,0}/\ cm^6\ molecule^{-2}\ s^{-1}) = -57.10 + 19.70 \log_{10}T - 3.410 (\log_{10} T)^2$, $k_{rec,¥} = 1.36 \times 10^{-10} \exp(-1020/T)$ $cm^3\ molecule^{-1}\ s^{-1}$, and $F_c = 0.67$.

CHEEK, G.T., Professor, "Electrochemical Studies of Diels-Alder Reactions in a Room-Temperature Molten Salt," *Electrochemical Society Proceedings*, (J. Yoshida, D.G. Peters, and M.S. Workentin, eds.), Volume PV 2001-14.

The Diels-Alder reactions of maleic anhydride and p-benzoquinone with cyclopentadiene have been carried out in the aluminum chloride: 1-ethyl-3-methylimidazolium chloride molten salt system. These systems have been found to produce the endo 1:1 adduct isomers in the basic and neutral melts, respectively.

CHEEK, G.T., Professor, "Electrochemical Studies of the Fries Rearrangement in a Room-Temperature Molten Salt," *Electrochemical Society Proceedings*, (J. Yoshida, D.G. Peters, and M.S. Workentin, eds.), Volume PV 2001-14.

The Fries rearrangement of phenyl benzoate has been studied in the aluminum chloride: 1-ethyl-3-methylimidazolium chloride (EMIC) molten salt system. Rearrangement occurs in 2 to 3 days in acidic and neutral buffered melts at 75°C and was not observed in basic melts. 4-Hydroxybenzophenone and 2-hydroxybenzophenone were obtained as major and minor products, respectively. Crossover experiments with benzene yielded only minimal amounts of benzophenone.

COPPER, C.L., Associate Professor, Prak, D.L., and Callahan, J.H., "Polycyclic Aromatic Hydrocarbon Metabolite Characterization by Capillary Electrophoresis and Mass Spectrometry," presented at the *Frederick Conference of Capillary Electrophoresis*, October 2000.

Capillary electrophoresis (CE) and mass spectrometry (MS) methods were optimized for analysis of compounds that are known metabolites of polycyclic aromatic hydrocarbon (PAH) biodegradation. Bacteria known to degrade PAH were employed in PAH biodegradation experiments performed in static or dynamic systems. Samples from these systems were screened for PAH metabolites using CE and MS methods. The presence of various known metabolites was confirmed and a structure of a previously unidentified metabolite of the PAH fluoranthene was proposed based on CE and MS results.

DeLONG, H.C., Major, (USAF) and Assistant Professor, co-author, "Recent Advances in Flame Retardant Polymer Nanocomposites," *Proceedings of Fire and Materials*, San Francisco, Jan 2001.

A new approach to address the ever-increasing demand for higher performance flame retarded products has recently focused on the use of mica-type clays nanodispersed in polymers. These "nanocomposites" exhibit the unusual combination of reduced flammability, in the form of lower peak heat release rates, and improved physical properties. The most important aspect of t the nanocomposite approach is the combined improvement in both flammability properties and physical properties. However, methods for preparation, which supply fully optimized nanocomposites, are still under development. Two important issues in this regard are: processing stability of the treated clays and quantitative measurement of clay dispersion. We report here on our recent efforts to address these issues. Specifically, using solid state Nuclear Magnetic Resonance (NMR) to evaluate clay dispersion and alkyl ammonium stability, and the use of thermally stable imidazolium treated clays.

De LONG, H.C., Major, (USAF) and Assistant Professor, co-author, "Polymer Layered-silicate Nanocomposites: Thermal Stability of Organic Cationic Treatments," *Proceedings of the Polymeric Materials Science and Engineering,* American Chemical Society, Washington DC, PMSE preprint, 83, 59-60, 2000.

The limited thermal stability of the alkyl ammonium cations and the processing instability of some polymers in the presence of nanodispersed montmorillonite have motivated the development of improved organophillic treatments for layered silicates. Success in this regard should enable preparation of polymer layered silicate nanocomposities from thermoplastic engineering polymers with high melt-processing temperatures and thermoset resins with high cure temperatures. Herein, we detail our efforts to address some of these issues. Our approach focuses on the use of new thermally stable imidazolium treated montmorillonite for preparation of nanocomposities. Several imidazolium salt derivatives were prepared with propyl, butyl, decyl, and hexadecyl alkyl chains attached to the imidazolium through one of the nitrogens. Complete spectroscopic, x-ray diffraction, and thermal characterization is presented. The use of 1,2-dimethyl-3-n-alkyl-imidazolium salt to replace sodium in the natural montmorillonite gives a 100ºC improvement in thermal stability as compared to the alkylammonium treated montmorillonite.

Technical Reports, Books and Book Chapters

HARRISON, J.A., Associate Professor, "A New, Reactive Potential Energy Function to Study the Indentation and Friction of *n*-Alkane C_{13} Monolayers," *Interfacial Properties on the Submicron Scale*, Frommer, J.E. and Overney, R., eds., ACS Press, Washington D.C., (2001), pp. 216-229.

The indentation and friction properties of *n*-alkane C_{13} chains chemically bound to a diamond (111) surface have been examined using molecular dynamics simulations and a newly developed potential energy function. Both a *flexible* and a *rigid* single-wall, capped (10,10) nanotube were used in the indentation and friction simulations. Gauche defects were formed during indentation of the C_{13} monolayer with both nanotubes. The flexibility of the nanotube, the depth of penetration, and the speed of indentation all affected the number of defects formed. Sliding simulations demonstrate that flexible single-wall nanotubes may not be suitable as scanning probe microscope tips for the study of tribology. Rupture of chemical bonds within the monolayer was possible during indentation and sliding under certain conditions.

WHITAKER, C.M., Assistant Professor**,** "Self-Assembly of Functionalized Rodcoil Molecules: Coatings for Superconductors, Photorefractive Composites, and Nonlinear Optical Materials," American Chemical Society, 44th Annual Report on Research, Petroleum Research Fund, August 31, 2000.

The design, synthesis and evaluation of molecules that self-assemble into novel, functionalized materials. Rodcoil oligomers containing rigid and flexible segments joined together ordered into supramolecular materials when cast as thin films. Our studies focused on improving the current understanding of the ordering behavior for oligomeric, organic-based systems and enhancing the magnitude of the second-order nonlinear optical response from bulk rodcoil materials.

Laboratory Experiments

METZ, P.A., Assistant Professor, "Separating the Components of Beach Sand," *Chemical Education Resources, Inc.*, ISBN 0-53497-727-8.

A mixture of sand, sea salt, and crushed seashells are separated and recovered. The mass percent of each component in the mixture and the total mass percent recovery are determined. Experiment Scenario: The Introduction to Glassmaking course at the State Art Institute is making soda-lime-silica glass from beach sand. The art professor needs assistance analyzing the mass percent of sand, sea salt, and seashells in beach sand she brought back from her summer vacation. The mass percentages are used to calculate the additional soda, lime, and silica needed to reach a target recipe. Students write a report of their finding to the art professor.

METZ, P.A., Assistant Professor, "Devising a Reduction Potential Table," *Chemical Education Resources, Inc.,* ISBN 0-53497-725-1.

Electrochemical cells are constructed from five different unknown metals and their respective metal salt solutions. The cell potentials are used to establish a reduction potential series for the five metals. Experiment Scenario: Intergalactic Mining Limited has discovered five new metals on the planet Metwen. The metallurgist needs help determining the reduction potential of each metal. Students build electrochemical cells from pairs of the metals. The cell potentials are used to establish a reduction potential series. Students write a report to the metallurgist detailing the logic they used to devise their series.

METZ, P.A., Assistant Professor, "Determining Hydrogen Peroxide Content by Gas Stoichiometry," *Chemical Education Resources, Inc.,* ISBN 0-53497-768-5.

The molarity and mass percent of hydrogen peroxide in a solution are determined by decomposing the hydrogen peroxide and measuring the oxygen produced. Experiment Scenario: A plant worker, fired by a vinegar company for making a dilution calculation error, has made a similar mistake at his new job with Global Hydrogen Peroxide. Assistance is needed determining the concentration of a batch of over-diluted swimming pool shocker to see if it can be salvaged as household hydrogen peroxide. Students write a calculation protocol for diluting any hydrogen peroxide solution to a specific concentration.

METZ, P.A., Assistant Professor, "Applying the Concept of a Limiting Reactant to the Synthesis of Aspirin," *Chemical Education Resources, Inc.,* ISBN 0-53497-777.

The most cost-effective limiting reactant for the synthesis of aspirin is determined. A sample of aspirin is synthesized and its percent purity is determined. Experiment Scenario: A college marketing course is working with Atkinson Health Products to explore the feasibility of adding aspirin to their product line. As part of this study a small amount of aspirin must be synthesized and its yield, purity, and cost of reactants determined. Students write a memorandum outlining their findings.

METZ, P.A., Assistant Professor, "Applying the Concept of a Limiting Reactant to the Synthesis of Aspirin," *Chemical Education Resources, Inc.,* ISBN 0-53497-819-3.

Predict whether a reaction will occur for each pair of eight ionic solutions. Given seven of the eight solutions as unknowns, combine pairs of solutions and observe results. Identify the unknown solutions and the missing solution. Experiment Scenario: Enviro Safe, Inc. received from the Biology Department seven, five-gallon carboys of solutions labeled Experiment 9. If the solutions are not identified, Enviro Safe will charge extra to dispose of them. The Biology Department knows eight solutions were used in the experiment and they need your help determining which are in the carboys and which is missing. Students write a memo to Enviro Safe detailing their analysis.

Presentations

BOWEN, C.W., Assistant Professor, "Overview of Common Statistics Used in Chemical Education Research: Analysis of Continuous Quantitative Data in Comparative and Experimental Studies," 16th Biennial Conference on Chemical Education, Ann Arbor, MI, August 2000.

BOWEN, C. W., Assistant Professor and METZ, P. A., Assistant Professor, "We Teach, But Do We Know that Students Learn?" National Science Teachers Association, Regional Meeting, Baltimore, MD, November 2000.

BOWEN, C.W., Assistant Professor, "Getting Started in Program Assessment and Evaluation," Chemistry Department, Towson University, Baltimore, MD, January 2001.

BOWEN, C.W., Assistant Professor, "Getting Started in Chemistry Education Research," Chemistry Department, University of Puerto Rico, Rio Piedras, PR, January 2001.

BOWEN, C.W., Assistant Professor, "Getting Started in Program Assessment and Evaluation," American Chemical Society, National Meeting, San Diego, CA, April 2001.

CHEEK, G.T., Professor, "Electrochemical Studies of Diels-Alder Reactions in a Room-Temperature Molten Salt," 198th Electrochemical Society Meeting, Washington DC, 28 March 2001.

CHEEK, G.T., Professor, "Electrochemical Studies of the Fries Rearrangement in a Room-Temperature Molten Salt," 198th Electrochemical Society Meeting, Washington DC, 28 March 2001.

CHEEK, G.T. Professor, "Diels-Alder Reactions in a Room-Temperature Molten Salt," 34th Middle Atlantic Regional Meeting, Baltimore MD, 30 May 2001.

DeLONG, H.C., Major (USAF) and Assistant Professor, co-author, "Polymer Composite Gel Electrolytes of Pristine and Lithium Containing Air Stable Substituted Imidazolium Ionic Liquids," NATO Advanced Study Institute, Molten Salts: From Fundamentals to Applications, Kas, Turkey, 3 – 14 May 2001.

DeLONG, H.C., Major (USAF) and Assistant Professor, co-author, "Electrochemical Behavior of Lithium Containing Polymer Gel Electrolytes of Air Stable Substituted Imidazolium Ionic Liquids," NATO Advanced Study Institute, Molten Salts: From Fundamentals to Applications, Kas, Turkey, 3 – 14 May 2001.

DeLONG, H.C., Major (USAF) and Assistant Professor, co-author, "Recent Advances in Characterization and Processing of Flame Retardant Polymer Nanocomposites, "Defense Applications of Nanomaterials," The American Chemical Society, Spring Meeting, San Diego, CA, 1 – 5 Apr 2001.

DeLONG, H.C., Major (USAF) and Assistant Professor, co-author, "Recent Advances in Flame Retardant Polymer Nanocomponents," Fire and Materials, San Francisco, Jan 2001

DeLONG , H.C., Major (USAF) and Assistant Professor, co-author, "Polymer Layered Silicate Nanocomposites: Thermal Stability of Organic Cationic Treatments," Fire and Polymers, The American Chemical Society, Fall Meeting, Washington DC, 20 – 24 Aug 2000.

DILLNER, Debra, Associate Professor, "Midshipman On-Line Laboratory System: A Web Based Approach to the General Chemistry Laboratory Manual and Laboratory Reports," 16th Biennial Conference on Chemical Education, Ann Arbor, MI, August 2000.

FERRANTE, R.F., Professor, co-author, "Radiation-Induced Conversions of Hydrocarbons in Environments Relevant to Pluto," 221st National Meeting, American Chemical Society, San Diego, CA, April 2001.

HARRISON, J. A., Associate Professor, "MD Simulations of Tribology of Hydrocarbon Lubricants," Gordon Research Conference, Plymouth, NH, July 2-7, 2000.

HARRISON, J. A., Associate Professor, "Molecular Dynamics Modeling of Scanning Probe Microscopy Experiments," 220th American Chemical Society National Meeting, New Orleans, LA, August 20-24, 2000. *(Plenary Lecture)*

HARRISON, J. A., Associate Professor, "Tribology of Alkane Monolayers: The Effects of Tip Flexibility and Defects," Fall Meeting of the Materials Research Society, Boston, MA, November 27- December 1, 2000.

HARRISON, J. A., Associate Professor, "The Tribology of Hydrocarbon-Containing Lubricants: A Molecular Dynamics Study," Adhesion Society 24rd Annual Meeting, Williamsburg, VA, February 25-28, 2001.

HARRISON, J. A., Associate Professor, "Molecular Dynamics Simulation of the Friction of n-Alkane Monolayers: Tip and Sliding Direction Effects," 221th American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

HARRISON, J. A., Associate Professor, "Effect of Packing Density on the Tribology of n-Alkane Monolayers," University of Wisconsin, Madison, WI, April 26, 2001.

HARRISON, J. A., Associate Professor, "MD Simulations of the Friction and Wear of Amorphous Carbon Coatings," AFOSR/ONR/NSF Tribology Review, Duck Key, FL, June 4-8, 2001.

HARRISON, J. A., Associate Professor, "MD Simulations of the Friction of n-Alkane Monolayers," AFOSR/ONR/NSF Tribology Review, Duck Key, FL, June 4-8, 2001.

HARTMAN, J.R., Assistant Professor, "Solid, Solution, and Gas Phase Structural Studies for a Series of Ni(II) and Cu(II) Complexes," Inorganic Chemistry at the Beginning of the New Millennium, Cambridge, MA, October 6-8, 2000.

KAMMIER, A.L., Midshipman 1/C, USN, and HARTMAN, J.R., Assistant Professor, "The Effect of Ligand Size and Denticity on Ni(II/III) and Cu(II/I) Redox Potentials," Eastern Colleges Science Conference, Wilkes Barre, PA, March 31, 2001. (Poster presented by Midshipman 1/C Kammier)

NASSIRI, J.D., Midshipman 1/C, USN, CHILDS, J.M., Midshipman 1/C, USN, and HARTMAN, J.R., Assistant Professor, "Synthesis and Study of a Series of Amine Functionalized Silica Gels Made Via the Sol Gel Process," Eastern Colleges Science Conference, Wilkes Barre, PA, March 31, 2001. (Poster presented by Midshipman 1/C J.M. Childs)

SCHROEDER, Maria J., Associate Professor, "Segmental Relaxation of Poly(styrene-co-vinylphenol) Copolymers," Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Maryland, 31 May 2001.

SHADE, J.E., Professor and Rest, A., "Synthesis and Matrix Isolation Studies of Isocyanide Iron Complexes," 220th National Meeting of the American Chemical Society, Washington, D.C., 20-25 August 2000. (Invited speaker)

Bitterwolf, T. E. and SHADE, J.E., Professor, "Photochemical Reactions of Cyclopentadienyl Metal Carbonyl Dimers with Hydrogen. Evidence for a CO-loss Intermediate in the Formation of Metal Hydrides," 220th National Meeting of the American Chemical Society, Washington, D.C., 20-25 August 2000.

TEICHERT, M.A., Captain (USAF) and Assistant Professor and Stacy, A.M., "Effects of Discussion Style on Students' Understanding of Chemical Bond Energy and Thermodynamics," American Chemical Society 220th National Meeting in Washington, D.C., August 2000.

WHITAKER, C.M, Assistant Professor, "Synthesis and Properties of Laterally Substituted Mesogens," American Chemical Society 220th National Meeting, Washington DC, August 22, 2000.

WHITAKER, C.M, Assistant Professor, "Self-Assembly Approaches to Molecular Electronic Devices," DARPA Moletronics II Program Meeting, Santa Fe, New Mexico, May 5-7, 2001.

WHITAKER, C.M, Assistant Professor, "Self-Assembly Approaches to Molecular Electronic Devices," DARPA Program Review, Naval Research Laboratory, Washington DC, May 2, 2001.

WHITAKER, C.M, Assistant Professor, "Programmed Assembly of Supramolecular Materials with Novel Optical Properties," Office of Naval Research Review for Optics and Electronics, Arlington, Virginia, June 11, 2001.