

## **CHEMISTRY 499**

### **UNDERGRADUATE RESEARCH**

Chemistry 499 provides a mechanism whereby undergraduate chemistry majors may participate in the research of the faculty and receive academic credit for that participation. While CHM 499 is usually taken by students in their senior year, it may be taken by juniors if the sponsoring professor feels that the student has had sufficient course work or previous work experience to be able to handle the specific project in mind.

Students interested in CHM 499 should begin by reviewing the attached list of projects. Following this, they should talk to the sponsoring professors about those projects which interest them to obtain further information about the projects and eventually reach a decision. After the student and sponsoring professor agree on a project and the number of hours of credit, it is only necessary then to register for the course in the usual manner. In this context, it should be kept in mind that three hours of laboratory work per week constitute 1 hour of credit. Hence, a student who elects 3 credit hours of CHM 499 should anticipate working 9 hours a week in the laboratory on his/her project.

At the end of the semester, two copies of a research report should be prepared, one for the instructor, and one to be kept on file in the Chemistry Office (specified by the American Chemical Society for accreditation purposes). The title page of the research report must include the project title, the student's and advisor's names, and the semester and year enrolled in CHM 499. The sponsoring professor has sole responsibility for determining the course grade. Please indicate the course grade on the Chemistry Office copy of the report. Should the work be published, the sponsoring professor will determine the extent of the student's contribution and, if appropriate, acknowledge the student's contribution in a footnote or else list the student as a co-author.

Some CHM 499 students may also choose to enroll in CHM 495, Seminar in Chemistry, either concurrently or subsequently, and give an oral presentation of their work. It should be emphasized, however, that this is strictly optional.

A final note. A number of our chemistry graduates who took CHM 499 reported that they found it indispensable in obtaining a job or in getting started on research in graduate school. Hence, it is highly recommended by the department as an elective.

Robert M. Berger

My research interests lie in the area of inorganic chemistry, particularly in the application of spectroscopy and electrochemistry to the characterization of transition metal complexes. Specifically, I am interested in the synthesis and characterization of transition metal complexes made up of an oxidizable metal center (such as Ru(II), Cu(I), Re(I), etc.) and ligands having low-lying  $\pi^*$  orbitals. These complexes typically have reasonably long-lived metal-to-ligand charge transfer excited states and may have applications in donor-photosensitizer-acceptor schemes.

### I. Design and Synthesis of Photoactive Complexes

Another area of interest is the design and synthesis of both mononuclear and polynuclear Ru(II) coordination complexes having long-lived MLCT excited states. Complexes containing from one to four metal centers may be prepared using bridging ligands such as 2,2-bipyrimidine(bpym); 2,3-bis-(2-pyridyl)pyrazine (dpp); and 1,3,5-tris-(2-pyridyl)triazine (tpt). The tpt ligand, shown to the right, is unusual in the sense that it may, depending on the orientation of the pyridyl rings, coordinate, up to three metal centers in a symmetric bidentate fashion or two metals unsymmetrically, one in a tridentate fashion and the other in a bidentate fashion.

Mononuclear and polynuclear ruthenium(II) complexes of tpt in which the tpt functions as a tridentate ligand (see figure) will be prepared. 2,2':6',2"-terpyridine (trpy) or a combination of a bidentate and monodentate ligand will be used to complete the coordination sphere of the metal center. Purification of the complexes will be carried out by ion exchange chromatography. The spectroscopic and electrochemical properties of the complexes will be investigated by the methods of electronic absorption spectroscopy, emission spectroscopy, cyclic voltammetry and bulk electrolysis.

### II. Preparation and Characterization of Donor-Photosensitizer-Acceptor Complexes

Recently I have become interested in the study of so-called donor-photosensitizer-acceptor complexes in which a photosensitizer (P) is covalently bonded to both an electron donor (D) and an electron acceptor (A). Absorption of light ( $h\nu$ ) promotes an electron from a lower energy orbital on the photosensitizer to a higher energy orbital (1) where it can begin an electron cascade (2,3) that ultimately results in a long range transfer from the donor to the acceptor. The photosensitizers are complexes of Ru(II) and Cu(I) with phenanthroline or bipyridine type ligands. The donors and acceptors are organic molecules with LUMOs and HOMOs of appropriate energies.

S. P. Coburn

### Isotope Tracer Studies of Pyridoxine Metabolism

The goals are to develop mathematical models which describe the kinetics of vitamin B-6 metabolism in vivo. The procedure is to measure vitamin B-6 compounds and the enzymes which metabolize them under various conditions in vitro and in vivo. Current emphasis is on metabolism in normal and malignant skin cells, development of techniques for using accelerator mass spectrometry, and improvement of mathematical models for describing vitamin B-6 metabolism. Involves analysis of blood, tissues, urine and stool specimens, HPLC, liquid scintillation counting, and compartmental modeling.

M. R. Columbia

### Additive Effects in Electrodeposition

My primary research interest is the electrodeposition of platinum from solutions containing chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) and how additives influence this. This arises from the decades-old practice of adding small quantities of lead(II) acetate to the plating solution to produce deposits of high surface-area platinum black, yet the role of the Pb(II) ion has never been firmly established. Films are deposited from solutions containing, as additives, the acetate or nitrate salts of Pb(II), Hg(II), Cu(II), Fe(III), Ni(II) or Zn(II), then studied using scanning electron microscopy and scanning tunneling microscopy to monitor their morphology and wavelength-dispersive X-ray spectrometry to determine their elemental composition.

### Development of Undergraduate Experiments for GC/MS and FTIR

A secondary interest is adapting reported research results as experiments which could be utilized in an instrumental analysis class. Current projects involve analysis of water for the presence of volatile aromatics via solid phase extraction and GC/GC-MS, and the study of thin polymeric films via specular reflectance FTIR.

R. J. Duchovic

### Computational Chemistry

The continuing rapid developments in computer technology (both hardware and software) have made available to the physical scientist extraordinary computational resources. The new hardware systems range from powerful desktop workstations to national networks of supercomputers. Combined with advances in operating systems and in programs designed for specific tasks, the current and future generations of computer technology have made computational science a co-equal partner with the traditional methodologies of theory and experiment in the natural sciences.

In addition to the rapid developments in computational ability, the past twenty years have witnessed important advances in specific areas of theoretical chemistry. More efficient computational algorithms have been proposed and tested which implement classical, semi-classical, and quantum mechanical formalisms. In particular, the elaboration of variational transition state theory and of new techniques to study quantum mechanical tunneling has had a major impact in the area of chemical kinetics. Further, new methods studying the transition from the ground state to excited states have permitted a more comprehensive examination of the dynamics of molecular collisions.

There are three broad research areas at IPFW in which the methodology of computational chemistry is applied:

#### CHEMICAL KINETICS

Projects in this area are centered on computing accurate estimates of the rates of chemical reactions. Currently, work is focused on reactions in the gas phase of small (3 - 10 atoms) molecular systems, particularly reactions which play a critical role in combustion processes. The

calculations require the application of various statistical rate theories to compute thermally averaged rate coefficients. These theories utilize concepts from statistical mechanics, ab initio quantum chemistry, and rovibrational spectroscopy.

## MOLECULAR DYNAMICS

In this area of research, projects attempt to study the microscopic dynamics of molecular collisions. Classical trajectory methods are used to investigate chemical reactions on model potential energy surfaces (PES) constructed from ab initio quantum chemical calculations and experimental data. These projects study energy partitioning among the products of a reaction and angular momentum constraints on the progress of a reaction. Finally, rate coefficients for the reaction are calculated from the trajectory data.

## AB INITIO CALCULATIONS/POTENTIAL ENERGY SURFACE MODELS

A central step in all dynamical studies is the characterization of the potential energy surface (PES) governing a chemical reaction. Projects in this area attempt to construct an analytic representation of the PES from available ab initio quantum chemical calculations and experimental information. The construction of these analytic functions requires the use of numerical techniques, abstract mathematics, and considerable ingenuity on the part of the investigator. In some situations it is necessary to do additional ab initio calculations.

K. L. Ericson

## Biochemical Protein Research

My research is in biochemistry, in the area of protein research. One project involves the purification of serine hydroxymethyltransferase (SHMT), that is involved in the production of purines and pyrimidines that make up the bases of DNA and RNA. It has been suggested that SHMT is a possible target for cancer therapy, as cancerous cells that are rapidly growing and dividing require more bases than normal cells. If the production of purines and pyrimidines is decreased, then these cancerous cells will not grow as quickly. The gene for the protein has been engineered into plasmid DNA of *E. coli*. Once purified from the bacteria, the protein's interactions with its co-factor, vitamin B-6 (pyridoxal) and the antagonist of pyridoxal, deoxy pyridoxine will be studied. In this way we hope to gain information on how SHMT might be targeted in cancer.

Another project is the production, purification and study of mammaglobin, a small protein that seems to be produced in breast cancer tissue. This project would involve the cloning of the gene into *E. coli*, expression and purification of the produced protein. Then the protein's interaction with the cell membrane and other parts of the cell could be studied.

For those interested in protein chemistry, the skills learned in cloning, expression and purification of a protein are essential for further education in the area of biochemistry.

R. S. Friedman

## Theoretical Physical Chemistry

The study of resonance phenomena is an extremely important area of research in the field of atomic and molecular scattering. From the simple elastic and inelastic atom-atom collisions to the more complex reactive scattering of chemical reactions, resonances play an influential role. We usually visualize resonances as quasibound or metastable molecular entities, for example, the intermediates of chemical reactions and even transition states of reactions. The existence of resonances is often the cause of marked variations in scattering cross sections or reactive transition probabilities; thus, resonances warrant careful examination. To study theoretically and rigorously resonance phenomena and scattering processes in general, we must use quantum mechanics and solve the Schrödinger equation, a second order differential equation. The research undertaken here is the analysis of quantum mechanical scattering processes via numerical (computational) studies of chemical reactivity.

Students engaged in such research will acquire a more detailed understanding of the mechanisms of chemical reactions (and scattering processes in general) as well as gaining valuable experience in computer use and numerical analysis. No previous programming experience is required.

### REACTIVE SCATTERING AND TRANSITION STATES

The availability of high-powered supercomputers and the development of very efficient numerical algorithms have made possible full three-dimensional quantum mechanical studies of simple chemical reactions such as  $\text{H} + \text{H}_2$  and  $\text{Cl} + \text{HCl}$ . Although these studies do not assume the existence of transition states (transient species composed of reactant atoms in a specific geometric arrangement which can then form the final products of a reaction), the studies can provide evidence of quantized transition states in the exact quantum dynamics. In fact, such quantized transition states are indeed seen and are dynamical bottlenecks which control chemical reactivity. The fundamental question posed in the study undertaken here of reactive scattering addresses the nature of quantized transition states: are quantized transition states reactive scattering resonances? An affirmative answer would imply that chemical reactivity can be described--at the ultimate quantum level of resolution--as a resonance phenomenon. This research involves solving the Schrödinger equation for one-dimensional models of chemical reactions using the computational resources available in the IPFW Chemistry Department. In particular, we are interested in looking at the simple hydrogen exchange reaction  $\text{Cl} + \text{HCl}$  to analyze the role of transition states in chemical reactivity. This work will also involve numerical fitting of potential energy curves for the chemical reaction.

### MULTIPLE POTENTIALS AND NONADIABATIC EFFECTS

A commonly-made assumption in chemical reaction dynamics is that, for a given chemical reaction, a single potential energy surface governs the chemical reactivity. Although this assumption is often valid, there are numerous systems of importance for which the interaction between two or more coupled potential energy surfaces must be considered. For examples, multiple coupled surfaces are necessary to describe photochemical reactions, electron-transfer reactions and Woodward-Hoffmann rearrangements. The effects of coupled potential energy surfaces on chemical reactivity, referred to as nonadiabatic effects, are often unknown. Studies of coupled potential energy surfaces in reduced dimensions, for example coupled two-dimensional

potential energy curves, can provide insight into this important area of research in chemical dynamics. In addition, whereas in one dimension, potential energy curves can not touch one another, in two-dimensions (and more) the potential energy surfaces can intersect in, what are called, conical intersections. These conical intersections have dramatic effects on chemical dynamics and are found in many chemical systems. The research undertaken here is to study in detail resonances arising from conical intersections of electronic potential energy surfaces.

## COMPUTATIONAL ALGORITHMS

There are a number of computational issues to consider when solving coupled differential equations arising from the Schrödinger equation. These include issues of numerical stability and linear independence. It is also instructive to compare different numerical integration schemes (e.g. Hartree, Numerov, and Gear) in terms of their computational efficiencies and error analyses. In collaboration with Michael Jamieson of the University of Glasgow, Scotland, we have been looking at a number of issues important in the area of numerical analysis.

D. E. Linn, Jr.

## Introduction

The field of transition metal polyhydridometallates,  $M/MH_n$ , has largely escaped the attention of the inorganic and catalysis community [1]. The richness of the preparative and reaction chemistry is such that it provides an ideal preparation for undergraduates wanting to pursue aspects of synthetic chemistry in their careers. Further, I would like to continue to explore this field due to the interesting chemistry of the metal-hydrogen bond and its role in a variety of the energy-related (e.g. batteries and fuel cells) and catalytic (e.g. hydrogenation) processes.

To stabilize these low oxidation numbers there is usually associated with this the electron-accepting properties of the ligands, i.e. there should be  $\pi$ -acid ligands with good acceptor orbitals. With hydrogen this mechanism is clearly not operative. Nevertheless, a number of very electron dense substances are known such as  $Mg_2NiH_4$ ,  $Mg_3RuH_3$ ,  $Na_2PdH_2$  and  $Mg_2RuH_4$  [2]. Here unexpected features such as metallic conduction and lattice defect structures are sometimes found. On the other extreme the high valent hydride is known,  $K_2[ReH_9]$ . The polarizability in the transition metal-hydrogen bond and lattice effects seem sufficient to show that there is immense flexibility in these materials to accommodate the variable electron density of the transition metal in the above complexes. This can be attributed to the polarizable transition metal hydrogen bond, which allows the hydrogen to accept a large radius away from the vicinity of the metal atom. According to Pearson's principle of maximum hardness there is a unique softness associated with  $H^-$  [3]. This ion has a low resistance to deformation of its electron density yet it has the highest ligand field strength of all the  $\delta$ -ligands [4].

Over the past seven years I have employed a number undergraduates as co-investigators and co-authors in papers concerning the solution chemistry of  $[FeH_6]^{4-}$  and  $[RuH_6]^{4-}$  [3, 5-8]. The rapid and convenient synthesis of  $[FeH_6][MgX(THF)_2]_4$  is achieved starting from iron halide and phenyl magnesium halide [5]. A good deal of work remains concerning the reactions of small molecules with these hydrogen and electron dense compounds. I would enjoy mentoring

undergraduates on some additional projects involving  $[\text{FeH}_6]^{4-}$  and perhaps one or two involving  $[\text{RuH}_6]^{4-}$ . The projects are of short enough duration and either reproduce or slightly expand upon work presently being done by undergraduates.

### Synopses of Undergraduate Research Topics

(1) Reactions of  $[\text{FeH}_6]^{4-}$  with unsaturated CN bonds. Our current work has shown that the reaction is accelerated by weak acids and occurs rapidly at room temperature. The product stoichiometry yields between one and two equivalents of primary amine (depending on nitrile) along with gaseous hydrogen. We are exploring ways to make this reaction catalytic and the role of acid catalysis. Catalytic hydrogenation is an important industrial reaction for the preparation of primary amines that could clearly stand improvement both from a "green chemistry" standpoint.

(2) Reactions of  $[\text{FeH}_6]^{4-}$  with organic carbonyls— Presently we have reactions that occur at room temperature and yield six equivalents of alcohol per iron. These reactions require no exogenous weak acids. There is an interest in expanding this study to include organic esters and carboxylates. These too are industrially relevant reactions.

(3) Chiral reductions using chiral  $[\text{FeH}_6]^{4-}$  complexes- The coordination sphere of the magnesium counter-cation can be bound to a chiral bis-binaphtholate ligand. Chiral NMR shift reagents allow the detection and analysis enantiomeric purity ( $\pm 3\%$ ) of chiral alcohols produced in this reaction. Should this reaction be highly successful it would also be extended beyond acetophenone to determine the scope of the reaction. Asymmetric catalytic hydrogenation is an important organic synthetic reaction currently being done in pharmaceutical industry.

(4) Hydrogenation catalysis using  $[\text{FeH}_6]^{4-}$  complexes— A limited number of turnovers is possible using gaseous deuterium as the reductant. It would interesting to determine whether the catalysis reaction can be extended through the use of exogenous phosphine ligands or higher hydrogen pressure.

(5) New hydrides complexes - Other new complex hydrides might be produced such as shown below.

Starting Materials for Preparations of Complex Hydrides,  $[\text{M}/\text{X}]_z[\text{MH}_n]$

Starting Complex:

COD = 1,5-cyclooctadiene Target Complex with M/  $\text{X}^+$  Type Counter-Cations

$[\text{Ni}(\text{COD})_2] [\text{NiH}_4]^{4-}$

$\text{CoCl}_2 [\text{CoH}_5]^{4-}$

$[\text{RhCl}(\text{COD})]_2 [\text{RhH}_6]^{3-}$

$[\text{IrCl}(\text{COD})]_2 [\text{IrH}_5]^{4-}$

Starting materials are simply prepared using reliable syntheses. For example, the olefin complexes of rhodium and iridium are readily prepared from the hydrates of RhCl<sub>3</sub> and IrCl<sub>3</sub> by refluxing 1,5-cyclooctadiene/ethanol [see below (M = Rh and Ir)] [9].



(6) Dinitrogen and arene reduction chemistry using [RuH<sub>6</sub>]<sup>4-</sup> complexes– The ruthenium complex appears to react with nitrogen in both solid and solution states. There is clear hydrogenation catalysis of arenes at room temperature. One of the goals is to determine if indeed this is the case and what the products are.

### Summary

These are a few lines of investigation available to undergraduate researchers. I always explain the topics to students and allow them to make their selections. Students with a biomedical orientation prefer the more organic synthetic applications such as chiral reductions. Students who desire a more industrial orientation tend to pick the catalysis projects.

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- V. M. Maloney

#### Zeolites as Active Supports for Hazardous Gas Sensors

Although many methods for the detection of hazardous or biologically important gases (eg. CO, CO<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>, and alkenes) have been developed for a wide range of applications, few have been commercially viable. One strategy for the detection of gases on the ppm level employs optochemical devices. These are based on an analyte causing changes in the absorption or emission characteristics of sensor molecules on a surface or embedded in a transparent solid. For example, the quenching of triplet excited states by oxygen is commonly used to determine oxygen concentrations in vitro.

#### Alkene Sensors

Alkene monomers used for the production of plastics such as acrylonitrile and methyl acrylate are often toxic, carcinogenic, and/or highly flammable. Threshold limits below 100 ppm have been set for various monomers. The decrease in the emission intensity of anthracene derivatives upon Lewis Acid catalyzed Diels Alder reactions with olefins could be used to detect these hazardous materials. Zeolites which are aluminosilicates with extensive networks of pores and channels can be prepared with Lewis and Bronsted Acid sites distributed throughout the interior. In this way, the zeolite would not only support the sensing molecules but catalyze the reactions for the detection of the analyte.

#### Carbon Monoxide Sensors

In the Gatterman Koch reaction, CO reacts with aromatic compounds in the presence of Lewis Acids to produce aromatic aldehydes. The absorption and emission characteristics of the product aldehydes differ significantly from the reactants. Pyrene embedded in acidic zeolites may react with CO to produce pyrenealdehyde whose formation can be detected by its emission. In each case, it may be possible to regenerate the original sensing molecules.

#### The Characterization of Phosphoryl- and Sulfonylnitrenes and their Application to Polymer Surface Modification

Nitrenes are highly reactive chemical species which have found applications in polymer crosslinking, surface modification, and photoaffinity labeling (used for mapping enzyme active sites). Sulfonylnitrenes and to a lesser extent phosphorylnitrenes have been used for these purposes due to their ease of preparation and high selectivity. To design effective agents for surface modification, further characterization of the photochemistry and reactivity of sulfonyl- and phosphorylnitrenes and their precursors is required. In particular, the reactivity of the singlet states and the conditions under which the sulfonylnitrene rearranges must be understood. Standard physical organic techniques such as product studies, matrix spectroscopy, and laser

flash photolysis will be employed. Ultimately, compounds will be designed and synthesized for modification of polymer surfaces.