

R.I.S.E. Workshop 2006



“I will lift up my eyes” – Gaelic

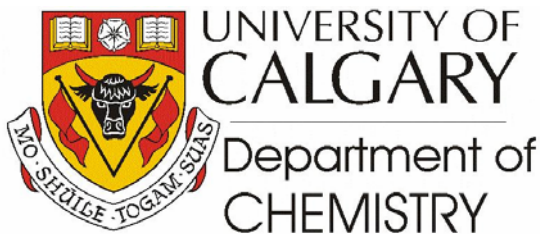
**August 25 – 26
University of Calgary**

Welcome

The year 2006 marks the 11th annual Reactive Intermediate Student Exchange workshop. We are very pleased to be hosting the workshop this year at the University of Calgary and being part of this wonderful tradition. When the program began there were 5 professors and 5 scholars from the universities of Dalhousie, Ottawa, Victoria, Waterloo and McMaster. Today the RISE program has 13 host institutions and since its inception the program has supported 120 dedicated undergraduate students. It is our sincerest hope that you enjoy this workshop and take the time to interact with your fellow students and supervising professors.

Thank you!

The R.I.S.E program would like to acknowledge the generous contributions from the University of Calgary, Department of Chemistry, Dean of Science and Catalyst Program. In addition we would like to extend our gratitude to NSERC for the supporting many of the students summer fellowships.



RISE Workshop Program

August 25 – 26, 2006

Friday August 25

Student registration in campus housing. Cascade Hall (CD) (see map)

6:00 – 8:00 pm

Wine and cheese welcome reception in Atrium in the Administration Building (A) on University of Calgary campus (see map)

8:00 - ?

Student excursion to local pub (optional)

Saturday August 26

Science B – Room 142

8:15 – 8:30

Welcome and opening remarks – Dr. Tito Scaiano

Chair: Kim Samkoe

8:30 – 8:55

Susan Ng – University of Calgary

8:55 – 9: 20

Esther Pierce – Université de Montréal

9:20 – 9:45

Matt Decan – University of Ottawa

9:45 – 10:15

Coffee break

Chair: Dr. David Cramb

10:15 – 11:00

*Guest Speaker – Dr. Matthew Lukeman
Acadia University
Department of Chemistry*

11:00 – 11:25

Katrina Traikov – University of Alberta

11: 25 – 11:50

Andrew Kitchin – University of Saskatchewan

12:00 – 1:30

Pizza lunch & Photos

Chair: Dr. David Cramb

1:30 – 1:55

Svetlana Kostina – University of Western Ontario

1:55 – 2:20

Sapphire Vanderlip – NRC Ottawa

2:20 – 2:45

Mohammad Sharif Askari – McMaster University

2: 45 – 3:15

Coffee break

Chair: Dr. Michelle Chretien

3:15 – 3:40

Michale Gaultois – Université de Montréal

3:40 – 4:05

Marija Antonic - Concordia University

4:05 – 4:30

Heather Wheeler –University of Toronto

4:30 – 4:45

Closing remarks – Dr. Willie Leigh

Evening

*Banquet – Eight Restaurant and Mercury Lounge
1530 5 St. S.W
Calgary, AB
(403) 806 – 0884*

AN INVESTIGATION INTO THE ABSORPTION SPECTRA OF PROTOPORPHYRIN IX AND VERTEPORFIN

Susan Ng^{*}, Kimberley Samkoe^{**}, William Meath^{***} and David Cramb^{**}

**University of Alberta, Edmonton, Canada*

*** University of Calgary, Calgary, Canada*

**** University of Western Ontario, London, Canada*

We are currently studying the phototherapeutic drugs Protoporphyrin IX (PPIX) and Verteporfin (VP), the latter of which is used in the treatment of age-related macular degeneration (AMD). In photodynamic therapy (PDT), a photosensitizer is excited and its subsequent relaxation may produce singlet oxygen, which can interact with various biomolecules leading to apoptosis of cells¹.

In this project, we determine the extinction coefficients and the transition dipole moments of PPIX and VP in various solvents and interpret the results with respect to the excited electronic state. The extinction coefficients are established using two different parameters (the absorbance values at the peak maxima and the integrated peak area) and we will compare and contrast the subsequent results.

INVESTIGATION OF THE METAL-SULFUR INTERACTION IN Pd(II) AND Pt(II) COMPLEXES OF 1,4,7-TRITHIACYCLONONANE BY PRESSURE-DEPENDENT LUMINESCENCE SPECTROSCOPY

Esther Pierce,* Geneviève Levasseur-Thériault, Christian Reber

**University of Toronto, Toronto, Ontario*

Université de Montréal, Montréal, Quebec

Extensive structural studies of Pt(II) and Pd(II) complexes of 1,4,7-trithiacyclononane (9S3), found in the literature, have shown an interesting long range axial interaction between the metal centre and the third sulfur of the 1,4,7-trithiacyclononane ligand. The nature and strength of this interaction is the subject of current debate.



In this project, Pd(9S3)Cl₂ and Pt(9S3)Cl₂ were synthesized according to literature procedures and the novel complexes [Pd(9S3)(en)][PF₆]₂ and [Pt(9S3)(en)][PF₆]₂ were synthesized and fully characterized. Luminescence spectroscopy was used to study these complexes at high pressures in the solid state. In contrast to simple square planar Pd(II) and Pt(II) complexes, the luminescence band maxima of which show a blue shift with pressure of approximately +25 cm⁻¹/kbar, the Pd(II) 1,4,7-trithiacyclononane complexes show a much smaller blue shift, on the order of +5 cm⁻¹/kbar, while the Pt(II) complexes show a red shift on the order of -25 cm⁻¹/kbar. We conclude that two effects are present – a blue shift due to equatorial ligand bond shortening and a red shift due to the approach of the axial sulfur to the metal centre. One effect or the other dominates depending on the metal and the ancillary ligand L.

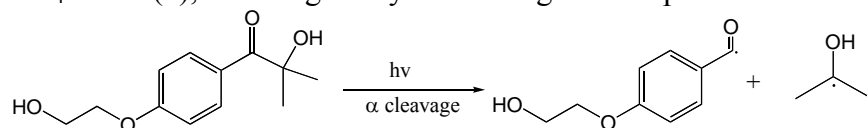
PHOTOSYNTHESIS OF UNPROTECTED GOLD NANOPARTICLES IN AQUEOUS SOLUTION

Matthew R. Decan^{*}, Katherine L. McGilvray, and J.C. Scaiano

^{*} On leave from: *The University of Western Ontario, London, Canada*

University of Ottawa, Ottawa, Canada

Stable, unprotected gold nanoparticles of 8-15nm in size were prepared in a simple, one pot, single step synthesis in an aqueous environment without the addition of stabilizing ligands. A photoinitiator was irradiated with UVA light producing ketyl radicals, which reduce H₂AuCl₄ to Au (0), initiating the synthesis of gold nanoparticles.



The optimal conditions and factors influencing the synthesis are discussed in detail. The synthesis of these nanoparticles was monitored by UV-VIS spectroscopy. TEM images of the particles were taken and analyzed to determine the range in size of the particles. The unprotected nature of these particles led to the study of possible interactions occurring between residual species and the gold nanoparticle surface. Feasible applications for the nanoparticles are also discussed.

DETECTING DNA DAMAGE USING MOLECULAR BEACONS AND REVERSE-PHASE MICROARRAYS

Katrina Traikov and Glen R. Loppnow,

Department of Chemistry, University of Alberta, Edmonton, AB, Canada

From the University of Western Ontario, London, ON, Canada

Target DNA strands were attached to epoxide-coated reverse-phase microarray slides via an imino linkage to see if thymine photoproducts and oxidative damage could be detected using fluorophore-labeled DNA hairpin probes. Thymine photoproducts were formed by irradiating the slides with 255 nm light. Oxidative damage was formed by irradiating the slides with UVA light in the presence of riboflavin. A decrease in fluorescence signal was observed with increasing irradiation times for both the thymine photoproduct and oxidative damage experiments. This decrease is attributed to damage of the target DNA strands resulting in weaker binding of the hairpin probes. Cross-binding of probes to non-complementary targets was found to be minimal. The effects of neighbouring bases in the formation of thymine photoproducts, the development of a positive probe for oxidative damage detection and the normalization of printing variations will also be discussed. These results demonstrate the feasibility of multiply-parallel photochemical studies on biomolecules.

RAFT Agent Photochemistry

Andrew Kitchin*, Ronald P. Steer**

**University of Calgary, Calgary, Canada*

***University of Saskatchewan, Saskatoon, Canada*

RAFT (reversible addition-fragmentation chain transfer) is a living radical polymerisation technique leading to low polydispersities and allowing for complex structures such as stars and blocks¹. The spectroscopic and photophysical properties of two common dithiobenzoate RAFT agents were investigated. Both agents were found to have fluorescence quantum yields on the order of 10^{-4} and maximum absorption bands at 300nm, assigned to the S_2 excited states.

The quenching of the model chromophore acenaphthene by a RAFT agent in solution and in a bichromophore was also studied. Quenching was found to operate via Förster resonance electronic energy transfer from the S_1 state of acenaphthene to the S_2 state of the dithioester RAFT agent. Time-correlated fluorescence lifetime measurements have been performed to determine the bimolecular quenching constant, k_Q , in ethanol to be $1.72 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

¹ G. Moad, E. Rizzardo and S.H. Thang, Aust. J. Chem., 58 (2005) 379

Effect of Ceramide in Model Raft Membranes: A TIRF Study

Sapphire Vanderlip, Ira, Linda Johnston

*University of Victoria, Victoria, Canada

***Stearie Institute for Molecular Sciences, National Research Council, Ottawa, Canada*

Lipid rafts are membrane microdomains enriched in tightly packed cholesterol and sphingolipids. They provide a liquid ordered phase microenvironment for membrane proteins in an otherwise fluid cell membrane. They are implicated in important cell signaling events. Their small size and dynamic nature make it difficult to visualize rafts directly in cell membranes. Enzymatic hydrolysis of raft Sphingolipid to give ceramide is thought to modulate their properties and functions.

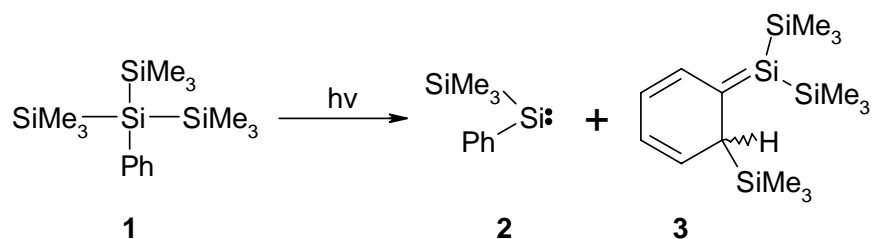
We followed the effect of in situ ceramide formation in model Sphingomyelin and cholesterol rich rafts using Total Internal Reflection Fluorescence (TIRF) microscopy and Atomic Force Microscopy (AFM). Fluorescent lipids were used to label the rafts and/or the surrounding fluid phase and ceramide was generated via the action of Sphingomyelinase. Fluorescence images indicate some restructuring in the bilayer and finer details from AFM images reveal increased heterogeneity in the individual rafts.

Characterization of a Transient Silylene and Silene in Solution by Laser Flash Photolysis of Phenyltris(trimethylsilyl)silane

Mohammad Sharif Askari and William J. Leigh*

* Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, ON, Canada L8S 4M1

The photochemistry of phenyltris(trimethylsilyl)silane (**1**) has been studied in solution by steady state and nanosecond laser flash photolysis techniques with the goal of detecting and characterizing the reactivity of phenyl(trimethylsilyl)silylene (**2**), which has been reported to be the major photochemical product from **1**. Photolysis of **1** in a 3-methylpentane matrix at 78K leads to the formation of a single species exhibiting $\lambda_{\max}=280\text{nm}$ and $\lambda_{\max}=665\text{nm}$, which has been assigned to **2** by previous workers¹. Flash photolysis of **1** affords two transients, one that exhibits $\lambda_{\max}=280\text{nm}$ and decays with $\tau=200-400\text{ ns}$ and another exhibiting $\lambda_{\max}=450\text{nm}$ and $\tau\sim 200\mu\text{s}$. The long-lived species was investigated in detail and assigned to silene **3** on the basis of its reactivity with various reagents and comparison of the data with those of closely related derivatives. The short-lived species reacts at close to the diffusion controlled rate with triethylsilane and methanol, and is tentatively assigned to silylene **2** on the basis of these results.



¹ S.G. Bott, Paul Marshall, P.E. Wagenseller, Y. Wang, R.T. Conlin, *J. Organomet. Chem.* **1995**, 499, 11.

CONTROLLED SYNTHESIS OF WATER SOLUBLE POLYMERS

Michael Gaultois, Nanaimo, Canada, Will Skene, Montreal, Canada.

Imine formation is an easy condensation between amino and aldehyde functionalized monomers to give polymers with tunable properties. Amino and aldehyde functionalized monomers were reacted to form water soluble polymers for potential use as hole injection layers.

Reactions were carried out at different concentrations to correlate concentration with molecular weight. Polymers were characterized by UV-Vis, fluorescence, and phosphorescence spectroscopies, as well as thermal gravimetric analysis, light scattering, cyclic voltammetry, and differential scanning calorimetry.

A model trimer was synthesized to decipher the polymer properties, and was further analyzed with laser flash photolysis.

ROLE OF GLYCERALDEHYDE-3-PHOSPHATE DEHYDROGENASE IN NITRATE TOLERANCE AND BIOACTIVATION OF GLYCERYL TRINITRATE

Marija Antonic*, Michelle N. Chretien**, Julie Laterreur**, Ann English**

* University of Ottawa, Ottawa, Canada

**Concordia University, Montreal, Canada

For over a century, the most common treatment for angina pectoris and cardiac failure has been glyceryl trinitrate (GTN). However, the rapid onset of GTN tolerance limits its clinical utility. It has been suggested that tolerance is caused by the inhibition of an enzyme that metabolizes GTN into physiologically active NO. Recently, mitochondrial aldehyde dehydrogenase (mtALDH) has been identified as one such enzyme.²

A related enzyme, glyceraldehyde-3-phosphate dehydrogenase (GAPDH) has also been observed to deactivate upon exposure to GTN.³ The goal of this project was to investigate a possible role for GAPDH in the bioactivation of GTN and nitrate tolerance. The effects of GTN on GAPDH dehydrogenase activity were studied with time and dose dependent enzymatic assays. Results show that with increasing GTN concentration and time exposure, the enzymatic activity of GAPDH is severely decreased. Mass spectrometry was then used to study the protein modifications on GAPDH due to GTN exposure. It was found that following GTN incubation, the GAPDH active site cysteines had been altered. Also, the ability of GAPDH to catalyze the formation of NO₂⁻ (regarded as the biological precursor to NO) from GTN was investigated using an HPLC-fluorescence assay. This revealed that GAPDH catalyzes the production of low concentrations of NO₂⁻ from GTN.

² Z. Chen, J. Zhang, J. S. Stamler, *PNAS*, **2002**, 99, 8306-8311

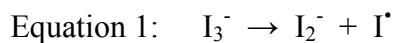
³ B. Jakschik, P. Needleman, *Biochem. Biophys. Res. Com.*, **1973**, 53, 539-544

Ultrafast photodissociation of solid state triiodide- sample preparation

Heather Wheeler, Ralph Ernstorfer, Robert E. Jordan, R. J. Dwayne Miller
Department of Chemistry, University of Toronto, Toronto, ON, Canada

Ultrafast electron diffraction is an extremely useful tool that makes it possible to visualize atomic motions in three-dimensional space with respect to time. This is referred to as “the molecular movie,” the making of which was the project goal. The molecular movie enables one to watch a chemical reaction as it happens, a feat that requires a time scale on the order of 100 femtoseconds (10^{-15} s)⁴.

The reaction of interest was the photodissociation reaction undergone by the triiodide anion (Equation 1)⁵.



Triiodide was chosen for a number of reasons. It is a simple, triatomic anion, making it relatively easy to study. It also has a number of unique characteristics. For example, it violates the octet rule and has excited electronic states below the electronic detachment threshold⁶. Furthermore, triiodide has broad absorption peaks centred at 290 and 350 nm², making it possible to use the readily available 266 nm light to induce the reaction.

The main task of the summer was to create a thin film of a triiodide-containing salt that is stable under vacuum. This task proved not to be trivial. At this point, such a film has not been successfully created.

⁴ Dwyer, J. R., Miller, R. J. D., et al. *Phil. Trans. R. Soc. A.*, (2006) **364**, 741-778.

⁵ Landrum, G., Goldberg, N., and Hoffmann, R. *J. Chem. Soc.*, (1997) **19**, 3605-3613.

⁶ Banin, U., Waldman, A., and Ruhman, S. *J. Chem. Phys.*, (1992) **96** (3), 2416-2419.