

“Theoretical Mechanisms and Kinetics of the abstraction reactions of fluorinated acetones by chlorine radical”

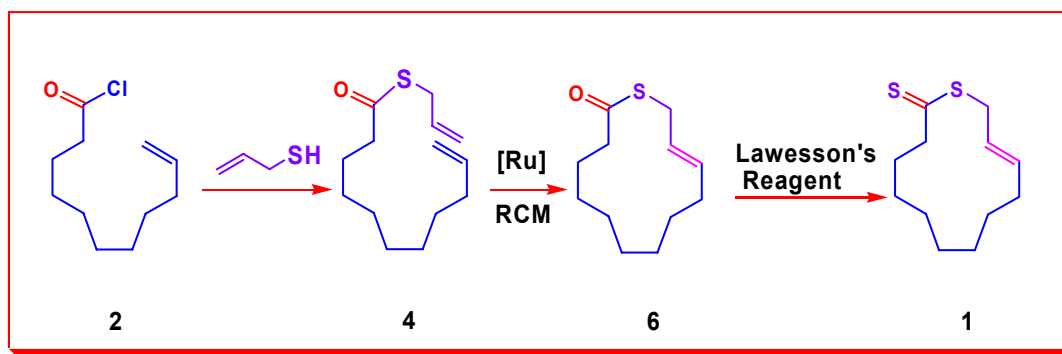
Huy Nguyen and Gerald Tiu, Troy High School, Fullerton, CA – 2005-06 National Team Finalists

Abstract: The mechanisms and kinetics of the hydrogen abstraction of hydrogen-containing fluorinated acetones (C_3H_6-xFxO , $x = 0-5$) by atomic chlorine are studied using density functional theory. These compounds are of particular significance because they result from the degradation of hydrofluorocarbons (HFCs), which are proposed replacements for chlorofluorocarbons (CFCs). Rate constants and optimized geometries for the reactants, transition state, and products are calculated for twelve different reactions involving different substituted acetones. The results reveal several trends to explain the behavior of these compounds in the atmosphere. Reactions were generally found to proceed slower as more fluorine atoms are substituted in the compounds. However, symmetric compounds and molecules that have singly fluorinated methyl groups were found to react faster than predicted. These trends are attributed to the unique properties of fluorine, including its high electronegativity, and could be extended to other volatile organic compounds and reactions with other common radicals, such as hydroxyl and nitrate. This work helps to clarify the mechanisms by which multi-halogenated compounds are oxidized in the troposphere, which is important in understanding the environmental fate of CFC alternatives.

“Macrocyclization using Ring-closing Olefin Metathesis: Synthesis of a 13-Member Dithiolactone”

Kiran Pendri, Choate Rosemary Hall, Wallingford, CT – 2005-06 National Finalist

Abstract: The synthesis of a novel 13-membered dithiolactone macrocycle (1) has been accomplished in three steps using thioesterification, ring-closing olefin metathesis (RCM) and thionation reactions. Ring-closing olefin metathesis reaction using Grubbs ruthenium catalysts was utilized for the crucial macrocyclization step affording the 13 member macrocyclic monothiolactone (6). Thionation of monothiolactone (6) using Lawesson's reagent gave the desired dithiolactone (1). During this work, we were able to demonstrate for the first time to our knowledge, olefin metathesis (CM and RCM) reactions on substrates having acid chloride and thio ester functionalities using Grubbs and Hoyveda guthenium catalysts. Thin layer and flash chromatography techniques were used for reaction monitoring and purification purposes. NMR, infrared, and mass spectroscopy techniques were used to characterize products.



“Synthesis and characterization of novel phenylbis (mercaptoimidazolyl) borates of manganese and zinc”

Bhaskar Mookerji, The North Carolina School of Science and Math, Durham, NC – 2004-05

National Individual Finalist

Abstract: The coordination chemistry of poly(mercaptoimidazolyl)borates has been used in developing synthetic models for active centered sulfur-rich metalloenzymes, and most recently, has been applied to the development of potential radiopharmaceuticals. We extend the study of these ligands to the largely uninvestigated phenylbis(mercaptoimidazolyl)borates, which utilize a phenyl substituent to inhibit terminal B–H bonds and have since been only coordinated to rhenium. A lithium salt of the novel phenylbis(mercaptoimidazolyl)borate anion $[\text{PhBm}^{\text{Me}}]^-$ has been synthesized by reaction of the lithium phenylborohydride with 2-mercapto-1-methylimidazole in THF. Under methanolic and aerobic conditions, treatment of $\text{Mn}(\text{CO})_5\text{Br}$ or $\text{Na}(\text{S}_2\text{CNR}_2) \cdot 3\text{H}_2\text{O}$ ($\text{R} = \text{Me, Et}$) and ZnCl_2 with $\text{Li}(\text{PhBm}^{\text{Me}}) \cdot \text{THF}$ produces manganese(I) tricarbonyl $(\text{PhBm}^{\text{Me}})\text{Mn}(\text{CO})_3$ and zinc dialkyldithiocarbamate $(\text{PhBm}^{\text{Me}})\text{Zn}(\text{S}_2\text{CNR}_2)$ ($\text{R} = \text{Me, Et}$) complexes. These complexes have been characterized using CHN elemental analysis; IR, ^1H , and ^{13}C NMR spectroscopies; and X-ray crystallography. We find *in solid state* the expected tridentate coordination in $(\text{PhBm}^{\text{Me}})\text{Mn}(\text{CO})_3$ and the common bidentate coordination of zinc Bm^{R} complexes in $(\text{PhBm}^{\text{Me}})\text{Zn}(\text{S}_2\text{CNMe}_2)$. These dithiocarbamate complexes are not only the first such PhBm^{Me} complexes to be structurally characterized, but $(\text{PhBm}^{\text{Me}})\text{Zn}(\text{S}_2\text{CNEt}_2)$ is also the first species having an unprecedented $[\text{ZnS}_4\text{H}]$ metal center due to a weak B–H \cdots Zn bridging interactions.

“Theoretical Mechanisms and Kinetics for the Reaction of Dimethyl Sulfide and Ozone in Water Vapor”

Angela Shih, Troy High School, Fullerton, CA – 2003-04 National Individual Finalist

The reaction mechanisms and kinetics for $\text{DMS} + \text{O}_3 \rightarrow \text{DMSO} + \text{O}_2$ in water vapor have been studied using density functional theory and a simple transition state theory. A series of reaction pathways was developed, and the results show that the activation energy decreases progressively as each water molecule is added to the reacting system. The decreasing energy changes are attributed to favorable electrostatic interactions between the reacting species and water. Rate constants for the second-order reactions involved different combinations of reactants hydrated with up to three water molecules and were calculated using simple transition state theory with Eckart tunneling corrections. Effective rate constants for the reaction have been obtained using the calculated second-order rate constants and the concentrations of hydrated reactants present in water vapor. The results show that the rate of reaction $\text{DMS} + \text{O}_3 \rightarrow \text{DMSO} + \text{O}_2$ increases dramatically in the presence of water vapor, which implies that the reaction of DMS with ozone can be significant in the troposphere and greatly influence the global climate.

Mentor: Dr. Fu-Ming Tao

“Synthesis and Oxidative Transformations Using Novel Water-Soluble Hypervalent Iodine Reagents”

Arun P. Thottumkara, Macomb High School, Macomb, IL – 2003-04 National Individual Finalist

Abstract: Selective oxidative transformations of functional groups are of paramount importance in synthetic organic chemistry. Hypervalent iodine reagents, such as Dess-Martin periodinane (DMP) and o-iodoxybenzoic acid (IBX), have found extensive use as mild and selective oxidizing agents, despite their limited solubility and shock-sensitivity. Herein, we report the syntheses of two new water-soluble and user-friendly hypervalent iodine reagents. The new reagents are shown to be chemoselective oxidizing agents for the oxidation of allylic/benzylic alcohols and the oxidation of benzyl ethers to the corresponding esters. Two plausible reaction mechanisms for these oxidative transformations have been proposed with the first step being an enthalpically favored H atom abstraction in both mechanisms. A Hammett correlation study conducted by the experimenter verifies the presence of a radical intermediate in the oxidation of alcohols to the corresponding carbonyl compounds. Additional mechanistic investigations have shown the reactions to be sensitive to the pH of the reaction medium.

Mentor: Dr. Thottumkara Vinod

“Synthesis, Deuterium Replacement, and Hydrogenation of the Compound HN(CH₂CH₂NHCOPh)₂”

Ishan Roy, Herbert Henry Dow High School, Midland, MI and Jason Becker, Wellington C. Mepham High School, Bellmore, NY – 2003-04 National Team Finalists

Abstract: The compound HN(CH₂CH₂NHCOPh)₂ was synthesized using a two step reaction: HOC₆H₄-NO₂-p + PhCOCl $\xrightarrow{\quad}$ PhCOOC₆H₄NO₂-p + HCl; PhCOOC₆H₄NO₂-p + HN(CH₂CH₂NH₂)₂ $\xrightarrow{\quad}$ HN(CH₂CH₂NHCOPh)₂ + HOC₆H₄-NO₂-p. This molecule was synthesized for its application in comparative studies amongst different bonding sites within a molecule, and for its potential as a precursor for a molecular “cage” that could be used for the complexation of metal anions. The focus of this experiment was on the reactivity of three different sites within the molecule, the benzene ring, the amide carbonyl group, and the amide and amine methylene groups. The compound was placed under mild, controlled conditions of temperature and pressure with H₂(g) and D₂O to observe the order of hydrogenation and hydrogen/deuterium replacement. This research revealed the hydrogenation of the benzene ring into a cyclohexyl group, followed by the hydrogen/deuterium exchange with the amine methylene occurring at 60-85psi and at temperatures less than 100oC.

Mentor: Dr. James Jackson

“H₂ Elimination from Y + C₂H₄”

Ann Chi, Terre Haute South Vigo High School, Terre Haute, IN and Irene Sun, Ben Davis High School, Indianapolis, IN – 2002-03 National Team Finalists

The study of transition metal-induced H atom and H₂ elimination in hydrocarbons aids in our understanding of the catalytic properties of metals on a very fundamental level. This research employed computational methods to analyze a representative reaction: the influence of Y on H₂ elimination from ethylene. Density functional methods (specifically B3LYP/aVDZ) and natural bond orbital (NBO) analysis revealed a three-step mechanism for the Y + C₂H₄ → YC₂H₂ + H₂ reaction. These steps include (i) YC₂H₄ adduct formation, (ii) C-H insertion, and (iii) H₂ elimination. The reaction was found to be exothermic (ΔH = -3.8 kcal/mol) with the insertion of Y into a C-H bond being the rate-limiting step.

Mentors: Dr. Eric Glendening and Daniel Wunderlich.

“The Synthesis of 1,2-bis(di-tert-butylphosphino) ethaneSupported Nickel(I) Silanes and Their Corresponding Nickel(II) Cations”

Michael Constantinidies, The University of Chicago Laboratory School, Chicago, IL -- 2002-03 National Finalist

Abstract: Transition metal complexes are important in organic synthesis and catalysis. Nickel usually has a formal +2 charge, although other charges are possible. Complexes containing a nickel atom with a +1 charge (called nickel(I)) and compounds containing a nickel-silicon bond (called silyls) are rare. A group of unique three-coordinate nickel(I) silyls and a corresponding nickel(II) silyl cation have been prepared. The preparation and spectroscopic characteristics of these novel compounds will be presented as well as an X-ray crystallographic study.

Mentor: Dr. Gregory Hillhouse

“The Isomerization of Quadricyclane to Norbornadiene Catalyzed by a Polymer-Supported Cobalt Porphyrin”

Gabriel Rosenhouse and Mark Saiget, Oregon Episcopal School, Portland, OR – 2001-02 National Finalists

Abstract: Cobalt porphyrin complex anchored to polyacrylonitrile fabric via an amide bond catalyzed isomerization of quadricyclane to norbornadiene with limited results. A promising sustainable residential heating system is the two-way photochemical isomerization of quadricyclane (Q) and norbornadiene (N). When exposed to sunlight and in the presence of an appropriate sensitizer, N transforms into Q. Q can then be catalyzed back into N, and this reverse isomerization releases a substantial amount of heat. By anchoring a catalyst onto an insoluble polymer, this reaction can proceed without the catalyst moving into the photochemical solution and preventing the buildup of Q during repetition of the photoisomerization step. In this study, tetracarboxyphenylporphyrin was synthesized and anchored to polyacrylonitrile fabric. Cobalt(II) was then complexed with the porphyrin and the resulting material successfully catalyzed the isomerization of Q to N. Gas chromatography on samples Q exposed to the catalyst indicates a 13% yield for the reaction, as compared with 26% and 17% yields for a homogenous control solution of Cobalt porphyrin. Further research on methods to increase the activity of the heterogeneous catalyst is being conducted.