Citizenship - Final Report

Citizenship Project

As stated in the citizenship project guidelines, the purpose of this project is to establish and foster collegial associations and collaborations with individuals both at BYU more broadly within my discipline. As an academic, establishing a network of scientists in my field who recognize my work and are excited about the potential outcomes of my research can be critical to the success of my research program. Thus, finding opportunities to establish and nurture these relationships is an important part of establishing a successful career and preparing for tenure. Below are some specific goals that will help me through the next year to foster these valuable associations with colleagues both inside and outside of BYU.

1. Specifically seek inside and outside reviewers for each of the grant applications and papers that I submit this coming year. It has been challenging for me to get my work outside of the university for review before submissions, but this could be a critical step not only for getting suggestions, but for helping others see and recognize my work.

2. Attend national conferences and mentoring workshops with the intent of fostering working relationships with individuals in my field. While I have attended conferences in the past, I will seek to take opportunities to find individuals that will review my work and with whom I can potentially collaborate. I will also do this at the NIGMS mentoring workshop I plan on attending in August of 2014.

3. Complete a new lab design project for enhancing Chem 455 with Dr. Matt Peterson. This project is aimed at introducing new and modern techniques and methods into an advanced Lab course to enhance student learning. Although I am not the instructor of the course, I am working together with Dr. Peterson in order to bring these new labs to fruition.

4. Observe teaching within the department and Invite colleagues to observe my teaching. While I have taken measures to improve my teaching, this goal will help me get meaningful ideas and feedback, and at the same time engage with colleagues in the department and establish the habit of discussing teaching with others.

5. Be a proactive member of the Recruiting committee. I will have the opportunity to travel to other institutions to recruit potential graduate students this year. My goal is to capitalize on these opportunities to establish relationships with individuals at these institutions. I will also be more proactive as a committee member in order to relieve the time commitments by senior members of the committee and take a more central role.

There are many activities that I currently pursue that compliment the specific goals I have outlined above. I review articles for peer reviewed journals, I serve as a member of the Reaxys guidance team with international peers, I regularly meet with colleagues to discuss research and teaching ideas and attend department seminars and journal clubs, and I am actively pursuing collaborative research projects with several faculty in the department. The goals outlined above will help me stretch myself in new ways, try new activities to improve my relationship with those inside and outside the university, and help me contribute in more meaningful ways to the community I am a part of.
1. Evaluate implementation of Scholarship Project:

   1. Seeking outside review of my grant applications and publications has forced me to add an additional step to my timeline. This means that I need to get the polished copy of my grant, specifically, completed earlier to allow time for external reviewers to give feedback and make corrections. This means that where my grant applications may have been good in the past, they are now more complete, clearer, and make more compelling arguments. This, should in time lead to greater success for funding.

   2. I attended an NIH mentoring workshop where I not only met program officers for the granting institution, but also experts in the field. From this experience, I have been asked to review manuscripts for the Journal of the American Chemical Society, which is one of the top journals in my field. Thus, I am considered an expert in certain areas, capable of reviewing the highest quality research. I also attended a Gordon research conference, which is a high impact conference in my discipline. Thus, I was able to communicate my early results and get feedback from experts.

   3. I completed a student research project aimed at improving teaching in a laboratory class in the department. Our modifications to the lab procedure were used a second time this year.

   4. I have not yet visited my colleagues lectures, or had colleagues review my teaching. It is scheduled for this semester, however, and I will be evaluated by a colleague. I do, however, talk extensively with colleagues about course preparation and get suggestions, ideas, and materials from several contacts.

   5. For the recruiting committee, I visited Utah State University and Idaho State University where I met with students and faculty and presented my research. I will make a similar visit this winter to Mexico (Puebla) in order to present my research and recruit potential graduate students. The thing that I have learned is that the quality of our graduate program is highly dependent on the caliber of students we have apply and are admitted. Thus, efforts to recruit good students can make our scholarship goals more realizable.
Scholarship Project - Final Report

Two critical components of establishing a successful research program at BYU are obtaining external funding and publishing my research in scholarly journals. These activities will enable me to establish a self-sustaining research program and help my students progress towards their advanced degrees in chemistry. The research goals outlined in the scholarship section of my faculty development plan will help me obtain these objectives, and include:

- Focus on mentoring undergraduate and graduate students by helping them to plan and direct their own research. Help them problem solve rather than solve their problems.
- Hold one-on-one research meetings weekly with each student to talk about progress, encourage greater personal development and support scientific growth that focuses on the light of faith.
- Present at a conference at least once per year (Gordon Conference)
- Attend NIH writing and mentoring workshop (accepted for August 2014)
- Write grant applications as follows:
  - External: NSF Career (July 2014), NIH R01 (October 2014), NIH Innovator (October 2014), Beckmann Foundation (September 2014), Air Force Young Investigator (September 2014), ACS PRF (November 2014)
  - Internal: MEG Grant, Graduate Studies recruiting grant
- Continue to get to know fellow faculty and explore opportunities to collaborate with Dr. Ess, Dr. Watt, Dr. Willardson, and Dr. Anderson
- Move research forward so as to publish a paper in a top-tiered journal on each of my projects each year.

As an early stage investigator in the chemical sciences, it is critical to initiate the process of obtaining outside funding through grant applications as soon as preliminary data allows. The experience of preparing grants and receiving feedback through colleague review and study group review can be helpful in shaping a research program in order to ensure future success with grant applications. My focus for the Scholarship Project will be to prepare and submit manuscripts for publications and grant applications that will enable me to obtain this critical feedback. Specifically, I plan to submit new applications to the NSF career program and to the NIH RO1 Program. These two new submissions will complement the proposals I have already submitted to various organizations and will continue to submit in the future. In addition, I plan to prepare and submit at least 2 research articles for publications based on work currently in progress. These initial publications and the experience gained through preparing new applications will position me well to secure funding in the future and establish a self-sustaining research program.

1. Evaluation, Experience, and Results:

Three themes characterize my goals associated with my scholarship goal: 1. Become a better mentor. 2. Get out into the chemistry community and make my research known; and 3. Move my research forward to concrete results (Publications and grant applications)

1. Improve mentoring. My focus during this period was improving the communication between myself and the student I mentor to ensure that they are obtaining the guidance and support they need to become good scientists. As I have met with students (graduate and undergraduate) on a weekly basis, I have become more aware of the issues they struggle with, and I have been able to
redefine their role and expectations on research in the laboratory. This has meant that I have lengthened the training period for new lab members, and been more thoughtful about what tasks I assign to which students.

2. I attended a research conference this past summer (2014) to present the initial findings of my research. As part of this, I contacted the chair to see if I could give a short presentation, and was given time for a short talk during the conference. Through this I met individuals with similar interests, and got my ideas out into the community to be evaluated. I also attended a NIH sponsored workshop where I met program officers and was able to get feedback from review panel members on how to prepare and sell my research in grant applications.

3. Productivity means getting things out, accepted, and funded. Thus, this past fall I focused on doing the necessary to get things out. With this focus, we submitted three manuscripts for publication in late 2014. One has been accepted and is published online in a peer reviewed journal, and two are currently undergoing peer review. This allows us to move projects forward and ask, what’s next?

I also prepared two new major grant applications that could serve as sustaining grants for my research program if they are awarded. The actual preparation of these proposals provided excellent opportunities to consider the direction and impact of our research, and has led us in new directions and towards exciting results.

Lessons Learned:
Through these goals I have learned a few important things that have become a part of my regular scholarship activities:

1. Understanding the capabilities and limitations of students comes through regular contact and communication. Training individuals requires that you know their level of expertise and the difficulty of assigned tasks. As I meet with students on a regular basis, I can see where they are struggling and help them develop specific skills. I also learn how to teach individuals to gain the skills they need.

2. A focus on the end product helps drive tasks in that direction. There came a point last semester where I realized we just needed to get things published and submitted. Thus, the focus became getting only the necessary information to obtain a finished product. Now that grants are submitted and papers accepted, we can move off in new directions and ask continuing questions.
Course Development Project - Final Report

Course Background

Chemistry 552: Advanced Physical Organic Chemistry. This is a graduate level course taught to the first year graduate students in organic chemistry and to senior and junior undergraduate chemistry majors interested in organic chemistry. Due to the small size of our graduate program, the course is generally dominated by undergraduate students (this past semester I had 3 graduate students and 9 undergraduates (3 juniors and 6 seniors)). Thus, the level of background is very diverse. Some students are learning topics for the first time. For others, many topics are review of previously learned information. Thus, there are challenges associated with the meeting each student's needs based on their background.

The course itself is a standard course taught at many universities that uses a standard graduate level text (Modern Physical Organic Chemistry, Anslyn and Dougherty). I was the only one teaching this class this year, and while I relied on the book organization, and materials from other instructors (including instructors from other universities) I created the content, assignments and tests. The course is a general survey of fundamental principles in organic chemistry that the students will use as a foundation for more targeted learning in the future. Thus, there is a need for students to be introduced to and understand a wide variety of topics and information upon which they can build throughout their graduate studies. Because this is an introductory graduate level course, I also emphasized the development of skills that will be useful to graduate level chemists, including computational chemistry, scientific writing, proposal preparation, and becoming familiar with the scientific literature.

Learning Outcomes

1. Predict relative energies and locations of frontier molecular orbitals for organic molecules of intermediate complexity using linear combinations of atomic orbitals and hybridized orbital approaches.
2. Perform calculations using ab initio, semi-empirical, density functional, and molecular mechanics approaches to predict energies and structures of ground and transition states.
3. Use reaction kinetics, linear free energy relationships, isotope labeling, stereo-electronic effects and stereochemical outcomes to determine reaction mechanisms.
4. Predict reaction mechanisms of major classes of organic reactions, including substitutions, eliminations, additions and radical reactions. Provide complete and correct arrow pushing mechanisms for these transformations.
5. Recognize the impact of non-covalent interactions in complex systems and reaction mechanisms.
6. Practice and improve critical reading and scientific communication skills through written and oral presentations of literature topics and through preparation of a fellowship application.

Quality and importance of learning outcomes:

1. The fundamental purpose of physical organic chemistry is to understand reactions and mechanisms to a level that allows a researcher to design and predict new reactions and reactivity of organic molecules. Thus, understanding bonding and the energy of electrons allows one to use that knowledge to study reactivity.
2. Computational chemistry is a tool for chemists that is growing in importance as the level of theory increases and cost of computations decreases. Thus, being able to understand the capabilities, limitations, and uses of computational chemistry, and to perform calculations at a certain level is a valuable tool for chemists to obtain during their training.
3. As organic chemistry is an experimental science, understanding the techniques used to study, understand, and investigate reaction mechanisms and factors that control reaction rates is invaluable. This broad understanding of reaction dynamics is broadly applicable to research in organic chemistry.

4. Understanding reaction mechanisms allows chemists to design new reactions, predict issues of selectivity and reactivity, and understand limitations associated with chemical structure or reactivity.

5. Interactions between molecules form the basis of structure in biological systems and in simple organic structures. Having a basic understanding of these types of interactions leads aids in the design and synthesis of new chemical structures and biological tools.

6. In addition to basic chemical knowledge and lab experience, communicating science both orally and in written form are essential skills for chemists in today's market. Thus, course activities focused on developing these skills right from the beginning or even before graduate school.

Course Activities

1. Computational chemistry assignment. Each student performed a computational assignment using Gaussian 09 to predict chemical structure and reactivity. This introduction provided specific examples of where computational chemistry can be used, its limitations, and specifics about using the techniques in chemical problems. Thus, each student became familiar with the methods of computational chemistry, making the area more approachable for later research.

2. NSF Graduate Fellowship Application. Each class member was required to prepare an application for a graduate fellowship. This assignment included multiple rounds of review and revision with other class members and various faculty members. The students not only got experience in writing and revision, but also got scientific input from myself and their research mentors. They also became familiar with the process of preparing and submitting a proposal, and with meeting specific requirements outlined in the grant instructions.

3. Out-of-class discussions: I held weekly out of class discussions where we went into further detail about concepts and provided a more in-depth view of topics. Similar to a recitation section, these focused on individual understanding of key topics. Next year they will be mandatory.

4. Out-of-class literature presentations. Reading the literature and being familiar with current research is a critical part of graduate research. Thus, this assignment required students to not only read a current article related to the course theme of physical organic chemistry, but to present the research orally, in summary, to discuss how specific physical organic tools were used to study a mechanism, and then to present generally how these tools are used in research. Feedback was provided from myself and from other class members on quality of presentation, clarity of research etc.

Assessments of Student Learning

1. Final report and revisions of NSF fellowship. The quality of writing was observed and steps taken to improve writing skills through a multi-tier revision process that included several different experts in the field. Final drafts where submitted to the funding agency for review when possible. Unfortunately, I did not keep copies of the final drafts to include in the appendix section. The process allowed students to go through multiple corrections and get feedback from experienced scientific writers, then revise their work accordingly. The final product of the proposal presentation was graded by myself as if I were a reviewer from the National Science Foundation. Comments included quality of presentation, the clarity of voice, the grasp of the scientific area, the quality of the candidate etc. This assessment allowed students to see how their application rated among fellow students preparing the same proposal application, to benchmark their potential to get funding from among their peers.

2. Homework sets: These provided students the opportunity to solve problems from the literature, explain reaction mechanisms with tools they had learned, and explain observations from the literature. Thus, the problems were literature based, real world situations that would require their knowledge of fundamental tools and techniques and phenomenon to solve. These problems often
required the student to do independent research and learning, and were above test level in difficulty. (See A.1)

3. Tests were given at 4 times throughout the semester to gauge students understanding of concepts and tools, and measure their ability to apply this knowledge to solving real world problems from the literature. Because these problems were generally related to scientific publications or real world problems, the correct application of these principles or concepts to the solving of these problems should translate into the students potential to solve similar problems in their actual research as graduate students. (See A.2 for a copy of the final)

Student Achievement of Learning Outcomes

From learning outcomes

1. From performance scores on the first exam, it was clear that the students understood the concepts related to molecular orbital theory and hybridization. Average score for test 1: 85%

2. Each student was required to independently run computer simulations of reaction mechanisms and use computational software to obtain structures and energies. The successful accomplishment of this assignment showed that students had a rudimentary understanding of how to run and interpret the computations.

3. The slightly lower average score from test #3 that covered kinetics and other physical organic chemistry techniques suggests that students struggled more with this section (77% average score). Several comments from the course evaluations mentioned that the amount of material was too high that was covered in this course. This may have contributed to the lower scores in this section. We covered many topics in less detail that could have been used. Thus, in future preparations, careful selection of the most important techniques and presentation of each topic in greater detail could lead to a higher level of comprehension and learning.

4. The students ability to predict reaction mechanisms and provide arrow pushing mechanisms was measured through performance problem sets and exams. These techniques were also developed in individual meetings with students outside of class where we reviewed and practiced specific mechanisms. The 70% average on the final exam suggests that students struggled to assimilate the large amount of information on mechanisms covered in the last portion of the class. This is also consistent with comments from students in their reviews about there being too many topics covered in the course. This will also be taken into consideration as the course is prepared for a second time.

5. While this was an initial goal of the course, due to the large amount of material available, this learning outcome was not pursued during the course.

6. Several of the out side of class activities/assignments for the course focused on developing these skills of scientific writing, reading and presentation. The high quality of final reports from the NSF application was evidence that students spent the necessary time and greatly improved their writing skills, or at least their approach to generating a high quality document. The excellent oral presentations on specific research topics presented by each student were also evidence that they grasped the tools used to study reaction mechanisms and could explain and understand how these tools are used and situations in which they can be appropriately used.

Steps Planned or Taken to Improve Teaching and Student Learning

I believe that the major concerns after analyzing student performance were that too much material/too many topics were covered in the course at the expense of going into further depth on any one topic. Students also commented on a lack of organization for the course. This may be related to the previous issue. I also felt that the students would have benefited from specific feedback about the quality of their literature presentations, and then had the opportunity to improve in a subsequent presentation.

Main goals for improving teaching and student learning are the following:
1. Carefully select the most relevant and important topics from each section of the course rather than striving to cover all topics. Thus, students will appreciate, understand, and retain better these most important topics as they have more opportunities to practice using each skill.

2. Provide more than one opportunity to give an oral presentation during the semester to measure how students improve their presentations based on feedback from the first presentation.

Appendix

A.1
Chem 552 - Problem Set 6
Fall 2014

Chapter 8
Readings:
Book Problems: 11, 12, 14, 19, 20, 21, 22

1. In a recent paper, results from $^{18}$F/$^{19}$F kinetic isotope effect measurements in SNAr reactions were reported. With heavy KIEs, secondary KIEs are rarely observed, and in this case only primary KIEs are important.

   A. $^1$H/$^2$H Primary KIEs are typically relatively large (<2). Why are these $^{18}$F/$^{19}$F KIEs so small?
   B. Draw the mechanism of the reaction of aniline (aminobenzene) with 2,4-dinitrofluorobenzene using the appropriate arrows to show electron flow.
   C. Describe which are the rate determining steps in reactions 1 and 2. Use the KIEs to provide a rationale for your answer.
   D. Draw an energy diagram (energy vs reaction coordinate) for reactions 1 and 2.

   E. Why are the rate determining steps different for the two reactions?

2. Provide a short explanation for the following kinetic isotope effects observed in the substitution reaction of the alcohol for a chloride (SN1).

   $X = \begin{array}{c|c|c|c|c|c|c|c|c} \text{Substituent} & \text{OMe} & 2927 & \text{CH3} & 19.69 & \text{C(CH3)}_3 & 13.12 & \text{Ph} & 5.076 & \text{F} & 1.859 & \text{H} & 1.323 & \text{Cl} & 0.3053 & \text{Br} & 0.2859 & \text{CF3} & 0.00837 \end{array}$

3. The solvolysis rates of $^3$-t-butyl-$^3$-methylbenzyl chlorides were measured in 80% aqueous acetone at 45 °C. The following rates were measured:

   $X = \begin{array}{c|c|c|c|c|c|c|c|c} \text{Substituent} & \text{OMe} & \text{CH3} & \text{C(CH3)}_3 & \text{Ph} & \text{F} & \text{H} & \text{Cl} & \text{Br} & \text{CF3} \end{array}$
A. Using Hammett $\rho$ values, calculate the $\rho$ value for the reaction. Is there a good correlation? Why or Why not?

B. Calculate the $\rho$ value using $\rho^+$ values. Is there a better correlation? Why or why not?

The reason this system was studied was to observe resonance effects when the cation intermediate can not achieve full conjugation with the benzene ring. The best correlation for this system comes from a combination of $\rho$ and $\rho^+$ values. These can be combined according to the equation $\log(k/k0) = \rho((1-r)\rho + r\rho^+)$ where $r$ equals 1.0 for a fully conjugated system. According to the authors of this study, $r = 0.91$.

C. Is there a better correlation between rates and the $\rho$ values using this equation?

D. Why is full conjugation not possible in this system? What would you expect the r value to be for $\text{-di-t-butylbenzyl chlorides}$? Greater or less than 0.91?

4. Using Hammett Parameters, calculate which of the following reactions will go faster and by how much. Be sure to show which parameters you are using. ($\rho$ = -1.31 for this system).

Provide complete arrow-pushing mechanisms for the following transformations. Provide an explanation for the observed selectivity, and provide the major product when appropriate.

1. 

2. 

3. 

4. 

A.2
Name_____________________________________________

Final EXAM
CHEMISTRY 552
Fall 2014

INSTRUCTOR: D. J. Michaelis
DATE: Thursday, December 18, 2014
MATERIALS NEEDED FOR THE EXAM: A pencil or pen and a calculator are all that is required. You may use models. You may use a calculator.
Please write your name at the top of this page.
If any answers are written on the back of a page, you must indicate it on the front of the page. Otherwise, the answer will not be graded. Please make your answers as concise and clear as possible. You will be graded not only on your answers, but also on the means by which you communicate them.

Relax, think and have fun.

1. (35 pts each). Provide a mechanism for each of the following transformations. If there is a certain selectivity obtained in the reaction (i.e. regioselectivity, diastereoselectivity), provide a rational for the observed product. Do only 7 of the 8 mechanisms.

a)

b)

c)

d)
2. (25 points each). Determining, explaining, and predicting selectivity is a hallmark of physical organic chemistry. In the following questions, you will be asked to provide models and transition states that explain and predict selectivity in a variety of transformations. Please ensure that your models are clear and easy to understand, and use transition state models to explain why certain products are formed in preference to others. Choose 4 of the following 5 problems (Everyone must do II).

I. a) Provide the major product and predict the selectivity for the reaction when the following substrate is heated. Provide an FMO analysis to explain why the observed product is formed.
b) For the above reaction, if the methoxy group was replaced by a methyl group, what product(s) would you expect to see and why?

II. a) Consider the following aldol reaction. When the starting ketone is treated with Li-TMP at -78 °C, a single diastereomer of the product is formed. Provide a mechanism for the transformation that explains what enolate is formed and why under these conditions, and provide a model for and predict which diastereomer of the product is formed. Does the product rotate plane polarized light?

b) The same ketone as shown above was then treated with NaOH at 0 °C and a single diastereomer was formed in this case as well. Provide a mechanism for the transformation that explains what enolate is formed and why under these conditions, and provide a model for and predict which diastereomer of the product is formed. Does the product rotate plane polarized light?
III. a) It is often stated that 4+2 cycloadditions are allowed, and 2+2 cycloadditions are forbidden (thermally). Provide an FMO analysis of the following transformations and show what is meant by allowed and forbidden.

b) The following transformation, although a 2+2 cycloaddition was shown to proceed thermally via a stereospecific, concerted process. Importantly, this reaction does not go via a concerted 2+2 with a twisted transition state, but rather through two separate pericyclic reactions. Provide a mechanism for the reaction (hint: The first step is a pericyclic reaction between the diene and the alkene of the ketene) and provide a name for each consecutive pericyclic reaction.

c) For the Diels Alder cycloaddition below, provide the major product of the reaction and explain why the regio- and stereoselectivity you predict are preferred. Also, provide a FMO analysis for this cycloaddition that describes which HOMO and which Lumo likely participates in the transformation.

IV. A significant advantage to photochemistry is that highly strained structures can often be generated via biradical pathways. Consider the following two reactions. Provide a name for each transformation. Provide 2 reasons why these structures form under photochemical conditions even though they are significantly higher in energy than the starting materials. A complete answer will include a discussion of excited states and a reaction coordinate diagram. Provide a rational for each reaction.

V. a) Draw transition states for the following transformations and predict the stereochemistry of the products. Draw the products in the linear form as shown and indicate favored stereochemistry.
b) For the Claisen reaction above, it was noticed that if a phenyl substituent was placed at the position indicated below, the reaction proceeded at much higher rates, even though the 3,3-sigmatropic rearrangement is known to proceed via a concerted mechanism. Explain this effect in terms of how concerted the reaction is.

3. (20) Provide oxidation states, d electron counts and total electron counts for the following complexes. For two of the complexes, provide the geometry of the complex and explain why it adopts this geometry. (COD = 1,5-cyclooctadiene)

Pd(OAc)₂
Ni(COD)(PPh₃)₂
IrCl₂(PPh₃)₃

4. (30 pts). Provide a mechanism for the following two transformations. (Hint: In A and B, a nitrogen nucleophile adds to an olefin that is bound to a Pd(II) center.) Name each step in these mechanisms.
5. (10 pts). In Reaction A above, when (t-Bu)3P is used instead of (n-Bu)3P, the reaction proceeds much faster. Provide a rational and explain what this tells us about the rate-determining step of the reaction. In reaction B, addition of Me3P instead of PPh3 leads to faster reactivity. Explain why. What does this say about the rate-determining step of the reaction?