

Application Form

Profile Information

Registration ID

[REDACTED]

Full Name

[REDACTED]

Date of Birth

[REDACTED]

Email Address

[REDACTED]

Pho

[REDACTED]

Address

[REDACTED]

Gender

[REDACTED]

Ethnicity

[REDACTED]

Language Preference

[REDACTED]

Legal Residence Information

Citizenship

[REDACTED]

Legal Residence Address

[REDACTED]

City

[REDACTED]

State

[REDACTED]

Zip Code

[REDACTED]

Your U.S. Congressional House District

Career Goals/Professional Aspirations

What is the highest degree you plan to obtain?

Ph.D.

In one or two sentences, describe your career goals and professional aspirations (see example below). This statement will be used in publications if you are selected as a scholar.

Ph.D. in Chemistry; I plan to conduct research in green chemistry to discover more efficient reaction frameworks while working to communicate chemistry more effectively.

What are your career goals and professional aspirations? Indicate which area(s) of mathematics, science, or engineering you are considering pursuing in your research career and specify how your current academic program and your overall educational plans will assist you in achieving your career goals and professional aspirations.

Following the completion of my bachelor's degree, I will enroll in a Ph.D. program in Chemistry, with the end goal of pursuing a career in either academia or industry. I intend to focus on green chemistry and educating the public on the importance of sustainability in science, technology, engineering, and mathematics. During my time as an undergraduate, I have spent time researching physical organic chemistry to better prepare myself for graduate school. I began conducting this research with the Sigman research group during my second semester of college alongside a postdoctoral research fellow and another undergraduate. Having only taken general chemistry, I had never been exposed to organic chemistry or electrochemistry, both of which were crucial aspects of my first project. Due to this, I had to overcome a steep learning curve; however, I was not deterred and persisted in learning these fundamental concepts. My first semester conducting research culminated in a symposium where I could practice communicating everything I had learned. While I was able to articulate everything I had learned in writing, verbally explaining the subject matter, and its importance, in a presentation format remained difficult. This experience encouraged me to push myself to grow and succeed as a researcher. I spent the following summer studying organic synthesis and learned that it is okay if experiments fail: The failed experiments provide us with as much insight as the successful ones. Since the publication of my first project in a high impact journal, I have worked on two additional projects, both computational in nature. Additionally, I worked as a Teaching Assistant (TA) for a General Chemistry lab course throughout the fall semester of my sophomore year. During the spring semester, I continued to TA for a graduate-level organic spectroscopy course focusing on training graduate students how to conduct and interpret various spectroscopic experiments. Both experiences helped me strengthen my knowledge of the subjects and helped me learn how I can better communicate chemistry. I recently completed two graduate-level courses: Physical Organic Chemistry I, and the subsequent Physical Organic Chemistry II. While these advanced courses are not required for the degree I am pursuing, my main goal in taking these courses is to apply the concepts I am learning in class to my research. I am enrolled in my university's Organometallic Chemistry graduate course this spring, which will help to further my knowledge of concepts that can aid me in the research I hope to pursue. The classes I have taken, and the TA positions I have held, reflect the time and effort I have devoted to growing as a student. Though it may prove difficult due to the COVID-19 pandemic, I hope to participate in an out-of-state research program during the summer of 2021 that will expand my breadth of knowledge, as well as further prepare me for my graduate studies.

Describe an activity or experience that has been important in helping shape or reinforce your desire to pursue a research career in science, mathematics or engineering.

“What does a scientist look like?” This question was addressed to a group of high school seniors who had just been accepted to the ACCESS Program for Women in Science and were about to enter their first year of college. The presenter went on to discuss that most children, when asked this question, would describe a male. My first year of college was spent as a member of the ACCESS Program and I often reflect on that initial question they presented to us. My current answer is that anyone can be a scientist, which is arguably one of the most important factors that has shaped my desire to pursue a career in research. An important aspect of this program is spending the summer before your first semester on campus taking a short course that emphasizes the amazing things researchers on campus have achieved. In addition to learning what a career in research entails, we discussed the varied experiences of women and minorities in STEM. Being able to listen to female professors, graduate students, and fellow undergraduates discuss their experiences with sexism shaped what I think a scientist can bring to the table. Prior to taking part in this program, I was unsure if I was the right type of person for a career in research. Being a first-generation student and a woman so passionate about countless subjects, I wondered if I could fill this role. However, through ACCESS, I learned that I could be both an activist and a scientist, simultaneously pursuing everything I am passionate about.

In what way did COVID-19 or other hardships affect your research career plans and did those events alter your ability to pursue those plans? If COVID-19 did not influence your plans, simply state that there was no effect.

Prior to the onset of COVID-19, I had intended to spend the summer of 2020 focusing on both computational and experimental work. As a result of social distancing guidelines and limited lab space, undergraduates at my university were unable to conduct experimental work over the summer. Due to this, my mentor helped me design a plan for a virtual project. While I did not expect to conduct an entirely computational project, I enjoyed learning new techniques and diving into a project I had worked extensively on in a completely different way. Conducting solely computational work from home, I ran into the issue of having a lot of free time while my computations were running. I reached out to my PI about this, and he recommended that I take on an additional project. I began working with another postdoctoral research fellow in the group and learned several other computational techniques allowing me to further expand my repertoire and explore new aspects of chemistry research. While I still believe there needs to be experimental support for the conclusions one draws from their computations, theoretical chemistry provides insights into systems that would otherwise be unavailable. The time I have spent conducting research during the COVID-19 pandemic has opened my eyes to how I can use computational chemistry to supplement the experimental work I plan to pursue in the future.

(Optional question, answering the question below will depend on your personal experience.) Goldwater Scholars will be representative of the diverse economic, ethnic and occupational backgrounds of families in the United States. Describe any social and/or economic impacts you have encountered that influenced your education - either positively or negatively - and how you have dealt with them or incorporated them in your work to reach your career goals.

When I was three years old, my parents separated. Growing up in a single-parent household impacted my view of the world. My father struggled to pay child support, and even though my mother worked tirelessly, we still relied on welfare to get by. We moved frequently and lived in various apartments, and it was not until my mother met my now stepfather that we were able

to live in a stable home. I often wonder where I would be if my mother had not met my stepfather. His support played a large role in how I have been able to achieve what I have. He encouraged me to explore my interests and to educate myself, as neither he nor my mom pursued education beyond a high school degree. Seeing my parents work tirelessly in jobs they did not enjoy just to support our family encouraged me to work hard and to find what I am passionate about. While I have always loved learning, I do not think I would have been able to excel academically if I continued living in a household where we struggled to make ends meet. I would have lacked the economic support to pursue an education and likely would have remained unaware of the fascinating science that describes our physical world. For this reason, accessibility in STEM is incredibly important to me and it is something I will always advocate for as I pursue my career in research: Everyone deserves to have access to science, regardless of their economic standing.

Research Projects and Skills

Research Project #1

Mechanistic Studies into the Oxidative Addition of Co(I) Complexes

Starting Month

01

Starting Year

2019

Ongoing

No

Ending Month

10

Ending Year

2019

Average Hours/Week (Academic Year)

12

Average Hours/Week (Summer)

40

Name of Project Mentor

Matthew Sigman

Position of Project Mentor

Peter J. Christine S. Stang Presidential Endowed Chair of Chemistry

Affiliation of Project Mentor

University of Utah

Name of Project Mentor

Shelley Minter

Position of Project Mentor

Dale and Susan Poulter Endowed Chair of Biological Chemistry and Associate Chair of Chemistry

Affiliation of Project Mentor

University of Utah

Name of Project Mentor

Christopher Sandford

Position of Project Mentor

Postdoctoral Research Fellow

Affiliation of Project Mentor

University of Utah

Institution where this research was performed

University of Utah

Description of research, including your involvement in AND contribution to the project. A separate narrative box has been provided for you to describe the research skills you acquired while working on this project.

Oxidative addition is a vital step in organometallic processes. Understanding the mechanism by which oxidative addition occurs provides insight into important cross-coupling reactions. I began my undergraduate research in the Sigman lab studying the oxidative addition mechanism of electrochemically generated pyridine-oxazoline-ligated Co(I) complexes into benzyl bromides. Throughout the Spring of 2019, together with another undergraduate, I measured oxidative addition rates with para- and meta- substituted benzyl bromides using cyclic voltammetry. Complicated Hammett relationships were discovered, so I spent the summer synthesizing deuterated forms of various benzyl bromides, as well as secondary and tertiary forms, and measured their rates to measure kinetic isotope and steric effects. Experimental and computational evidence led to the conclusion that a halogen-atom abstraction mechanism was occurring. This work was published in November 2019 and inspired a current project.

Research Skills (Briefly describe any research skill(s) you developed while working on this project that will be important going forward in your research career.)

I received comprehensive training in electroanalytical techniques, particularly cyclic voltammetry, to study trends in reactivity. I am substantially trained in organic synthetic techniques, including analysis of NMR and IR spectra, and purification and characterization of products.

Do you have Papers/Publications associated with this research project?

Yes

If yes, how many publications are associated with this work?

1

Citation

Sandford, C.; Fries, L. R.; Ball, T. E.; Minter, S. D.; Sigman, M. S. Mechanistic Studies into the Oxidative Addition of Co(I) Complexes: Combining Electroanalytical Techniques with Parameterization. *J. Am. Chem. Soc.* 2019, 141, 18877–18889.

Status

Published

How are you listed in the publication?

Author [REDACTED]

Type of Publication

National Professional Society Journal

Do you have Presentations associated with this research project?

Yes

If yes, how many presentations are associated with this work?

1

Citation

Sandford, C.; Fries, L. R.; Ball, T. E.; Sigman, M. S. "Using Electroanalysis to Determine Trends in Oxidative Addition Rates". Poster session presented at: 2019 ACCESS Research Symposium; 2019, April 19; Salt Lake City, UT.

Campus, Regional, National or International

Campus

Presentation type

Poster

How are you listed on the presentation?

Presenter

Additional Research Projects and Skills*Research Project #2*

Computational Analysis of Katritzky Pyridinium Salts

Starting Month

01

Starting Year

2020

Ongoing

Yes

Average Hours/Week (Academic Year)

10

Average Hours/Week (Summer)

40

Name of Project Mentor

Matthew Sigman

Position of Project Mentor

Peter J. Christine S. Stang Presidential Endowed Chair of Chemistry

Affiliation of Project Mentor

University of Utah

Name of Project Mentor

Christopher Sandford

Position of Project Mentor

Postdoctoral Research Fellow

Affiliation of Project Mentor

University of Utah

Institution where this research was performed

University of Utah

Description of research, including your involvement in AND contribution to the project. A separate narrative box has been provided for you to describe the research skills you acquired while working on this project.

After studying the oxidative addition of pyrox-ligated Co(I) into benzyl bromides, we wanted to understand how changing the substrate altered the mechanism. Katritzky pyridinium salts were an ideal choice as they are stable and easily synthesized electrophiles that function under various conditions, often undergoing a radical decomposition process. In order to study the decomposition of Katritzky salts, I have calculated the reduction potential for these species bearing both electron-donating and electron-withdrawing groups. Electronic and steric DFT-level properties were obtained for ground-state conformations and are being used to model the reduction of these compounds. Additionally, I computed transition states for homolytic cleavage of the C-N bond in the pyridinium substrates. The data I collected will be used in collaboration with the Watson Group (University of Delaware) to understand how the introduction of different substituent groups affects radical cross-coupling reactions.

***Research Skills** (Briefly describe any research skill(s) you developed while working on this project that will be important going forward in your research career.)*

This project provided me with a thorough understanding of computational techniques, such as the use of density-functional theory (DFT) computations to obtain molecular properties. I use these properties as parameters in multivariate-linear regression models, which I construct and analyze via MATLAB.

Do you have Papers/Publications associated with this research project?

No

Do you have Presentations associated with this research project?

No

Additional Research Projects and Skills

Research Project #3

SAPT as a Tool for Studying Non-Covalent Interactions

Starting Month

06

Starting Year

2020

Ongoing

Yes

Average Hours/Week (Academic Year)

15

Average Hours/Week (Summer)

40

Name of Project Mentor

Matthew Sigman

Position of Project Mentor

Peter J. Christine S. Stang Presidential Endowed Chair of Chemistry

Affiliation of Project Mentor

University of Utah

Name of Project Mentor

Jacquelyne Read

Position of Project Mentor

Postdoctoral Research Fellow

Affiliation of Project Mentor

University of Utah

Description of research, including your involvement in AND contribution to the project. A separate narrative box has been provided for you to describe the research skills you acquired while working on this project.

Noncovalent interactions (NCIs) are often analyzed with costly, lengthy density-functional theory (DFT) transition-state analysis. An approach combining linear free energy relationships with cost-effective computations would provide substantially more information about the effects of NCIs in organic reactions. Symmetry-adapted perturbation theory (SAPT) describes NCIs in terms of electrostatic, exchange, induction, and dispersion energetic components. I

have used this method to study anion- π interactions between halide anions and variously substituted benzene rings. SAPT component breakdowns have been compared with total interaction energies and electrostatic potential with the goal of understanding patterns in substituent effects. I am continuing this study by comparing other NCIs to the results I have obtained with anion- π interactions. SAPT is also being employed to study a kinetic-resolution experiment to understand if there are benefits to using SAPT over DFT.

***Research Skills** (Briefly describe any research skill(s) you developed while working on this project that will be important going forward in your research career.)*

I have expanded my skills in computational chemistry as a result of working on this project, as I can now analyze and submit SAPT computations alongside DFT computations. I have become more familiar with python and other coding languages in addition to efficient literature searching techniques.

Do you have Papers/Publications associated with this research project?

No

Do you have Presentations associated with this research project?

No

Mentor Recognition Information

Mentor Name

Matthew Sigman

Title

Dr.

Mentor Name

Shelley Minteer

Title

Dr.

Mentor Name

Christopher Sandford

Title

Dr.

Other Activities and Accomplishments

Activity/Accomplishment

Green Chemistry Committee

Organization (if applicable)

American Chemical Society

Scope of Activity/Accomplishment

College/University

Role/Involvement

The Green Chemistry Committee's main goal has been to implement a glove recycling program in the Chemistry department. My role has been to educate on the program's importance and recruit volunteers via social media.

Leadership Position

Social Media Manager

Length of Involvement

Academic Year

Additional Other Activities and Accomplishments

Activity/Accomplishment

Project Youth

Organization (if applicable)

Bennion Center

Scope of Activity/Accomplishment

College/University

Role/Involvement

As part of this program, members traveled to predominately low-income elementary schools to discuss their higher education experiences with fifth and sixth graders. This was done to encourage the pursuit of an education.

Leadership Position

Mentor

Length of Involvement

Semester

Additional Other Activities and Accomplishments

Activity/Accomplishment

ACCESS Mentor

Organization (if applicable)

ACCESS Program

Scope of Activity/Accomplishment

College/University

Role/Involvement

I have been an ACCESS mentor for two summers, in-person (2019) and virtually (2020). I helped students build a support system they could depend on during their first semester of

college and advised them on the process of entering a research lab.

Leadership Position

Mentor

Length of Involvement

More than one academic year

Additional Other Activities and Accomplishments

Activity/Accomplishment

Science Fair Coordinator

Organization (if applicable)

Canyons School District

Scope of Activity/Accomplishment

Community

Role/Involvement

I volunteer at a local elementary school to plan and engage in assemblies that advertise the science fair and encourage students to participate. I teach students the scientific method, judge their projects, and present awards.

Leadership Position

Volunteer

Length of Involvement

More than one academic year

Recognitions

Recognition

ACCESS Scholarship Recipient

Type

College/University

Award Description

A scholarship program that provides support for freshmen and transfer students from a variety of backgrounds pursuing degrees and careers in STEM. Students enter research labs during their first spring semester, culminating in a research symposium.

Award Year

2018

Additional Recognitions

Recognition

President's Scholarship

Type

College/University

Award Description

Recipients for this full-ride scholarship are chosen from a pool of high-school seniors that are residents of Utah. Selection is based on academic excellence.

Award Year

2018

Additional Recognitions*Recognition*

UROP Award Recipient

Type

College/University

Award Description

Provides undergraduate students the opportunity to submit a research proposal for review. Once it has been approved, students are awarded a monetary stipend to work on their proposed project and attend research education events.

Award Year

2019

Additional Recognitions*Recognition*

Mack Thomas Rozelle Scholarship

Type

College/University

Award Description

A monetary award granted to students excelling in Organic Chemistry courses.

Award Year

2020

Additional Recognitions*Recognition*

Undergraduate Research Award

Type
College/University

Award Description
Recognition of students involved with undergraduate research in the Chemistry department.

Award Year
2020

Current College/University

Institution type:
4-year institution

Are you a transfer student (i.e., Did you transfer from another academic institution to the institution that is nominating you for a Goldwater scholarship?)
No

Field of study
Chemistry

Chemistry areas of specialization
Chemical Catalysis

Period through the end of which you will be reporting your GPA
Fall 2020

Official cumulative unweighted GPA through the period reported above
3.90

How many credit hours does your school require for graduation?
122

How many credit hours will you achieve as of January 1, 2021?
144

How many credit hours do you plan to achieve for graduation?
182

Expected baccalaureate graduation month
05

Expected baccalaureate graduation year
2022

According to the definition provided above, indicate whether you are a sophomore or junior.
Junior

Matriculation status at the institution you will be attending during the 2021-2022 academic year

Currently Enrolled

Have you been involved in or do you plan to Study Abroad?

No

Coursework

Current Course 1

Biological Chemistry I

Course Level

Undergraduate

Current Course 2

Quantitative Chemical Analysis

Course Level

Undergraduate

Current Course 3

Physical Organic Chemistry I

Course Level

Graduate

Current Course 4

Physical Organic Chemistry II

Course Level

Graduate

Future Course 1

Organometallic Chemistry I

Course Level

Graduate

Future Course 2

Inorganic Chemistry

Course Level

Undergraduate

Future Course 3

Quantum Chemistry

Course Level

Undergraduate

Future Course 4
Thermodynamics and Kinetics

Course Level
Undergraduate

Future Course 5
Advanced Organic Chemistry Lab

Course Level
Undergraduate

Future Course 6
Advanced Inorganic Chemistry Lab

Course Level
Undergraduate

Course outside of Major 1
Partial Differential Equations

Course Level
Undergraduate

Course outside of Major 2
Applied Complex Variables

Course Level
Undergraduate

Course outside of Major 3
Statistics

Course Level
Undergraduate

Previous Schools attended

Future Academic plans

Is the institution you will be attending for the 2021-2022 academic year the same as your current academic institution?

Yes

Certification and Release

Applicant's Signature

[REDACTED]

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Mechanistic Studies of Oxidative Addition with Co(I) Complexes

Catalytic processes in chemical reactions function by providing an alternative reaction pathway with a lower activation energy and are essential for the efficient synthesis of numerous indispensable compounds, including medications, pesticides, and petrochemicals. Transition-metal catalysts are often used in organic coupling reactions and most commonly facilitate three main steps: oxidative addition, transmetalation, and reductive elimination (Figure 1). The mechanism by which the first oxidative addition step occurs can be highly dependent on substrate/ligand combinations. Knowledge of these substrate/ligand effects on oxidative addition could allow for the prediction of reactivity; therefore, we theorized that elucidation of the unknown mechanism of activation of benzyl bromide substrates by Co(I) complexes bearing pyridine-oxazoline (pyrox) ligands would enable us to gain knowledge into substrate/ligand effects on oxidative addition, which could allow for the prediction of new reactivity with alternative substrates.

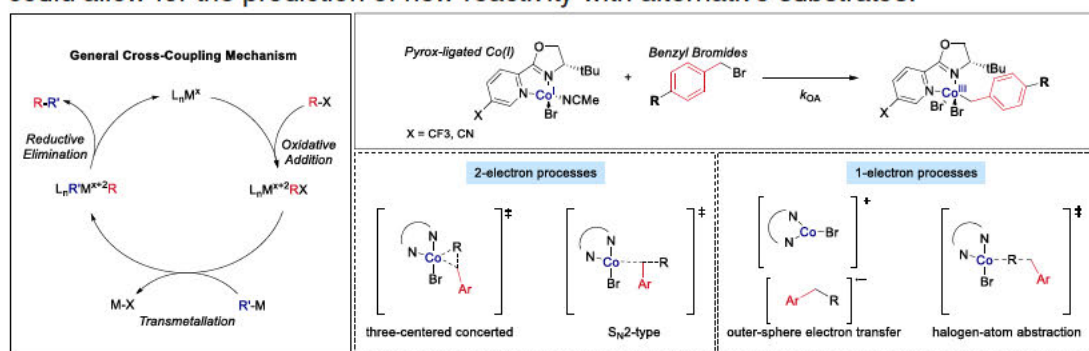


Figure 1: General cross-coupling and oxidative addition mechanisms.

Oxidative addition involving cobalt is thought to proceed through one of four mechanisms: three-centered concerted oxidative addition, S_N2 -type oxidative addition, outer-sphere electron transfer, and halogen-atom abstraction (1) (Figure 1). A Hammett study serves as a useful tool to differentiate between the possible reaction mechanisms. We applied this analysis to our study of oxidative addition, in which we measured the effects of varying substituents at *para*- and *meta*-positions of the benzyl bromide reactant on reaction rate.

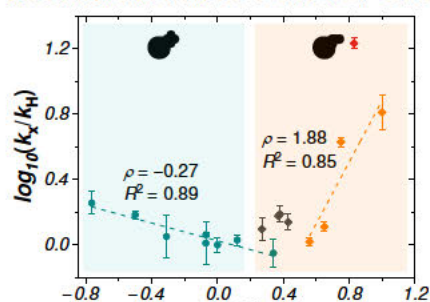


Figure 2: Broken Hammett plot.

In collaboration with another undergraduate researcher, I used cyclic voltammetry to measure reaction rates for the addition of pyridine oxazoline-ligated Co(I) into benzyl bromides. Throughout the spring of 2019, we measured oxidative addition rates for seventeen benzyl bromide substrates, which were used to create Hammett plots for each of a variety of pyrox ligands. Hammett plots traditionally exhibit a linear trend based on the electronic properties of the substituents being analyzed, but the plots we constructed revealed a V-shaped trend in substituent effects (Figure 2) for all ligands tested. An observable break exists in the plot around $\sigma = 0$ as substituents switch from electron-donating to electron-withdrawing groups, suggesting a change in the

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oxidative addition mechanism between electron-rich and electron-poor substrates.

As we began to probe this unusual trend the following summer, I collected the majority of the experimental data, while my colleague focused mainly on computational studies. I first investigated the effect of increasing substrate concentration on peak potentials, as measured via cyclic voltammetry (CV). Both my experimental data and digital simulations conducted by my mentor suggested a multi-step reaction, in accordance with the broken Hammett plots, as well as the existence of a discrete carbon-centered radical. As a consequence, we ruled out two-electron concerted processes in favor of processes involving a carbon-centered radical intermediate.

Due to differences in the resulting radical's stability, reaction rates of secondary and tertiary benzyl halides can be measured to distinguish between one-electron mechanisms. I synthesized and tested secondary benzyl bromides, which reacted faster than their primary counterparts, suggesting a process in which increased substitution stabilizes the formation of a benzyl radical. I also measured a consecutive increase in rate moving from primary benzyl chlorides to their secondary and tertiary analogues (Figure 3). This line of evidence pointed toward a halogen-atom abstraction mechanism, which directly forms a benzylic radical. Conversely, an outer-sphere electron transfer process would become more challenging upon the addition of an electron-donating methyl group that raises the LUMO energy.

Further support for a halogen-abstraction mechanism was provided by kinetic isotope effect (KIE) studies. I synthesized and tested deuterated analogues of *para*-CN benzyl bromides (Figure 3), with one and two deuterium nuclei replacing the benzylic protons. Measured secondary KIE values were large and above

the theoretical maximum of ~ 1.4 (2), indicating that not only are the measured values influenced by a change in hybridization during the rate limiting step, but by an additional equilibrium isotope effect. Alongside the evidence I collected experimentally, our team conducted various computational studies that supported our hypothesis of a halogen-atom abstraction mechanism. Subsequent to determining the mechanism of oxidative addition, we were able to develop a model using multivariate-linear regression techniques that could predict benzyl halide reactivity with Co(I) based on the particular substrate/ligand combinations, which was published in a high-impact journal (3).

More recently, I have extended the study to explore the impact of using a new electrophile class that I believed could expand our knowledge of oxidative addition involving Co(I) complexes, namely Katritzky pyridinium salts. These salts are particularly interesting to us because they were utilized as radical precursors in a Ni^I/Ni^{III} catalytic cycle by Watson and coworkers in 2017 (4). I synthesized multiple Katritzky pyridinium salts, and my initial CV studies with Co(I) and pyrox ligands revealed that these salts are irreversibly reduced in the electroanalytical window in which cobalt oxidation occurs.

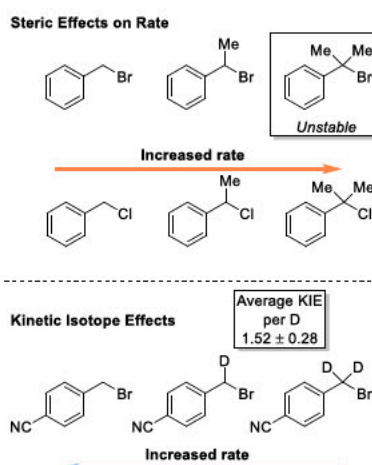


Figure 3: Steric and isotopic effects.

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Experimental evidence has also demonstrated that radical decomposition is only irreversible in the presence of 2,6-phenyl substituents (5). A radical decomposition step is postulated to be involved in the oxidative addition mechanism with Co(I) (Figure 4), so I began a computational analysis of substituent effects on kinetic and thermodynamic properties, as well as reversibility, of the radical decomposition.

Following the onset of COVID-19 in the spring of 2020, which limited laboratory access, I began learning a variety of computational techniques to apply to this project. Throughout the summer of 2020 I computed reduction potentials and ΔG^\ddagger for the cleavage of the C_{benzylic}-N bond of various pyridinium salts using density-functional theory calculations. I determined that the addition of electron-donating methoxy substituents to the para position of phenyl rings and removal of the phenyl ring para to the nitrogen made the salt more difficult to reduce, resulting in a more negative reduction potential. Somewhat unexpectedly, the introduction of electron-withdrawing trifluoromethyl groups did not make these substrates easier to reduce. My computational studies revealed that trifluoromethyl-substituted pyridiniums differ from methoxy-substituted pyridiniums in that they are more likely to retain π -stacking interactions

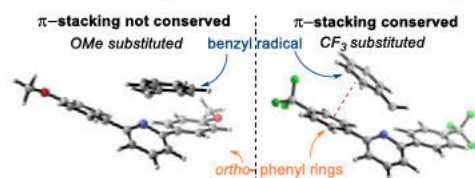


Figure 5: π -stacking in transition states.

between *ortho*-phenyl rings and the benzylic group in the radical intermediate and into the transition state (Figure 5). Larger ΔG^\ddagger values and more negative reduction potentials upon removal of 2,6-phenyl rings indicates a more reversible radical decomposition, as reported by Grimshaw and coworkers in 1983 (5). The reason for this is still unknown, as the data I have collected does not indicate that π -stacking results in a less reversible radical decomposition and there does not seem to be a concrete trend in ΔG^\ddagger values, so further work to understand this is ongoing.

I am currently employing multivariate-linear regression to model the effects of substituents on the reduction potentials of Katritzky pyridinium salts and we have instigated a collaboration with Dr. Mary Watson (University of Delaware) to determine if the compounds I have calculated to be more difficult to reduce will be more efficient in their Ni^I/Ni^{III} catalytic cycle. The study of substrate/ligand effects on the oxidative addition step of cross-coupling mechanisms has so far enabled the prediction of reactivity and has the potential to be applied to the design of new catalytic systems. I hope to expand my ability to develop and test hypotheses as I continue to study this system.

- 1) Diccianni, J. B.; Katigbak, J.; Hu, C.; Diao, T. *J. Am. Chem. Soc.* **2019**, *141*, 1788.
- 2) Streitwieser, A.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.
- 3) Sandford, C.; Fries, L. R.; Ball, T. E.; Minter, S. D.; Sigman, M. S. *J. Am. Chem. Soc.* **2019**, *141*, 18877.
- 4) Basch, C. H.; Liao, J. X.; Piane, J. J.; Watson, M. P. *J. Am. Chem. Soc.* **2017**, *139*, 5313.
- 5) Grimshaw, J.; Moore, S.; Trocha-Grimshaw, J. *Acta. Chemica. Scand. B.* **1983**, *37*, 485.

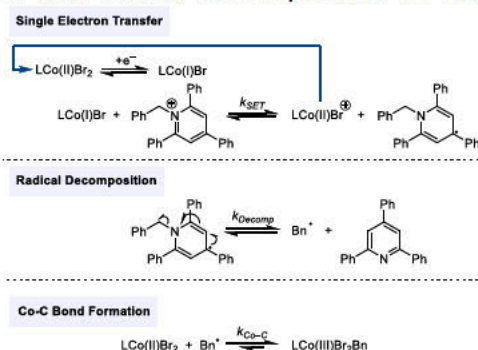


Figure 4: Oxidative addition of Katritzky salts.