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INTERSECTIONS OF ENVIRONMENTALISM, CHEMISTRY, AND RACISM:
AN EXPERIMENTAL STUDY OF HALOBENZENE HYDROGENOLYSIS

AND CRITICAL COMMUNICATION STUDIES OF
EQUITABLE LEARNING PRACTICES
ROOTED IN BLACK FEMINISM

By
Lauren Olivia Babb
B.A. Barnard College of Columbia University, 2018

A THESIS
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science
(in Chemistry)

The Graduate School
The University of Maine
August 2022

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An Abstract of the Thesis Presented
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Increasing concentrations of fluorinated aromatic compounds in surface water, groundwater, and soil pose threats to the environment. Fundamental studies that elucidate mechanisms of dehalogenation for C-X compounds (where X represents a halide) are required to develop effective remediation strategies. For halogenated benzenes, previously published research has suggested that the strength of the C-X bond is not rate-determining in the overall rate of dehalogenation. Instead, the rate-determining step has been hypothesized to be adsorption of the C-X compound onto the surface of a catalyst. Building on this hypothesis, in this work, we examine the reaction kinetics of fluorobenzene conversion to benzene, catalyzed by 5% Rh/Al₂O₃. The study here includes evaluation and optimization of experimental methodology, collection of initial rate data across a range of reactant concentrations and identification and numerical modeling of potential elementary reaction steps. We hypothesize that reduction of the rhodium (Rh) surface is required for the conversion of fluorobenzene to benzene and that pretreatment of the catalyst under ambient temperature and pressure with H₂
improved data reproducibility more amenable to detailed theoretical treatments. Preliminary analytical work supports this hypothesis.

In addition to the analytical work that centers this Master of Science thesis in Chemistry, this thesis contains two additional components (abstracts below) with direct bearing on STEM instruction and pedagogy: (1) an evaluation of the impacts of systemic racism on undergraduate chemistry education (Babb, L. and Austin, R.N., 2022. Chemistry and Racism: A Special Topics Course for Students Taking General Chemistry at Barnard College in Fall 2020. *J. Chem Ed.* 99 (1): 148-153); and (2) the piloting of a new course Black Feminist Thought and Education [CMJ493/PAX498/WGS410] (Babb, L.; Herakova, L.; Roberge, K. Academic Spaces of Possibility? 2022. A Proleptic Dialogue with BlackFeminism at the Center. *Feminist Pedagogy*, accepted for publication) at University of Maine that invited direct inquiry into practices of how we engage in ‘educating’.

Chapter 3 of the thesis summarizes the work published in “Chemistry and Racism A Special Topics Course for Students Taking General Chemistry at Barnard College in Fall 2020”. To explore the myriad ways in which systemic racism diminishes chemistry, and to recommend changes to our home department, a seminar-style course was created that provided a structured venue in which to collaborate with students. The course was created by the department chair, after reflecting on the Black Lives Matter message that it was time for white people to do some of the work to educate others about systemic racism. This relatively low stakes course (only one credit, pass/fail grading mode) successfully created a space for intense conversation, reflection, increased understanding of some of the aspects of racism in chemistry, as well as the impetus for institutional change. A description of the course, along with student opinions and co-facilitator reflections, are presented.

Chapter 4 of the thesis summarizes the work published in “Academic Spaces of Possibility? 2022. A Proleptic Dialogue with BlackFeminism at the Center”.
This critical commentary engages our experiences as co-educators in a “Black Feminist Thought and Expression” (BFTE) course, first-of-its-kind at our predominantly white institution in the U.S. We imagine and provoke redefinitions of “classrooms” and “students” toward the liberatory dialogic learning bell hooks continues to inspire. We reflect on the potentials and perils of BFTE as pedagogical moves toward 1) becoming learners over and over again and 2) creating multiple different learning spaces, not confined to the physical classroom or to texts-as-usual. By bringing our beings together in both this essay and in BFTE, we re-member the dialogic pedagogy of love-as-action hooks advocated for: involving the complexities of our unique positionalities, their impacts, and our shared commitments to each other and to learning rooted in both the intimate wisdom of the personal and in critical analysis of the social. As co-authors, we identify with divergent academic fields, genders, races, ages, nationalities, and institutional roles. Engaging our differences and coming together, we sought to “change our teaching practices, talk to one another, collaborate in a discussion that crosses boundaries and creates a space for intervention” (hooks, 1994) to center Black Feminism as knowledge, transformation, joy, and care.
DEDICATION

To my village. Thank you for growing me into the woman I am today.


Rachel Narehood Austin, PhD. Brian Frederick, PhD. Thomas Schwartz, PhD. Karen Merritt, PhD., MPH. Maria Blankemeyer. David Liao, PhD, Jacob Austin. Andrew Boucher & family.
Liliana Herakova, PhD & family. Kevin Roberge & family. Shontay Delalue, PhD. Lisa Neuman, PhD. William Gramlich, PhD. Laura Cowan, PhD. Bridie McGreavy, PhD. Tony Sutton, PhD.
Rachael Williams and her grandmother, Beryl Elisabeth Warner Williams, PhD.

ACKNOWLEDGEMENTS

Mom, Dad, Rebecca, and all my family/friends thank you for always reminding me that I am enough.

To the members of my committee for showing me a path forward. To Dr. Austin for reminding me to measure twice and cut once. To Dr. Schwartz who taught me you can only measure a rate within a factor of two. To Dr. Merritt who taught me to take what I need and leave the rest behind. To Dr. Frederick whose patience and care is the backbone of this thesis.

To Amirali Zangiabadi Ph.D. for High Resolution Transmission Electroscopy Microscopy imaging and Matthew Klein Ph.D. for assistance with Micromeritics H₂ chemisorption data collection.

Finally, to future readers, I hope this thesis supports you in your pursuit of knowledge.
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1.1. Research motivation for hydrogenolysis of halogenated benzenes

In my second semester of UMaine, the world was told to go home and stay inside. I was officially starting as a member of the UMaine Catalysis group, and the labs were closed until it was deemed safe to begin research once again. My time at UMaine taught me the importance of thinking globally and acting locally. Through isolation, I was determined to connect to the local community to explore issues that intersected science, social justice, and equitable learning opportunities.

Amid the global pandemic that disproportionately impacted Black, Latinx, and Native Americans, I initially grappled with feelings of powerlessness under quarantine. In this time of physical isolation, I connected with a UMaine alumni, who grew up on Indian Island, Lokotah Sanborn. In a conversation about community health concerns and the impact of Covid-19 on the reservation, he asked me one question that focused the trajectory of my chemistry master’s degree. “Have you heard about the history of dioxins in the Penobscot River?”

Immediately, I began to read about common pollutants from available EPA/WHO/UNICEF resources on-line and from historical accounts in local newspaper clippings. Water pollution remains a major scientific and technical problem, and few effective, low-cost catalysts have been developed to break down halogenated organic compounds, a major source of industrial pollution. These pollutants in drinking water affect millions of people across the United States, particularly marginalized communities living adjacent to waste sources.

Dioxins, PBCs, PFAS, and poly-fluorinated aromatics were a few of the halogenated compounds that were of interest to me because there was a great need for more comprehensive fundamental research on the elimination of these compounds in the environment.

During isolation, I contacted the Department of Natural Resources Water Resources
Program of the Penobscot Nation. Their mission is to protect and restore the quality of water used by the tribe. They report water advisories and monitor pollutants such as dioxins. I spent weekends on rivers across Central/Northern Maine, collecting water samples that were sent to government facilities for testing. While on the water, I was able to learn more about the spiritual aspects of water for Indigenous communities. I had read essays about the historical context of environmental equity between humanity and nature. But being on the water listening to the elders of the community tell stories of the centuries of performing ceremonies in the river and how pollutant advisories has changed in the past few decades was a transformative experience.

In addition, my co-advisor Thomas Schwartz had been interested in dehalogenation chemistry since the beginning of his career at UMaine. Our mutual interest in the science and the local impact of this research topic, the creation of a Graduate Student Fellowship and subsequent NSF proposal came to be. The core philosophy of heterogenous catalysis at UMaine is the research group's commitment to sustainability and green chemistry processes. I wanted to conduct experiments aimed to close the gaps in our understanding of how to remediate halogenated aromatics.

This impact of sustainable science clearly benefits our planet, in addition, there is a seamless application to address inequities faced by marginalized communities.

I also learned that simply caring about a social problem was not sufficient to position myself to be an effective problem-solver, even when I had the technical tools. I spent some of my time in graduate school co-teaching courses that provided me with the opportunity to practice skills that make me better at communicating with others and more comfortable with social differences that can be difficult to surmount but that ultimately need to be surmounted to work with others to find practical solutions to environmental problems that will be accepted and implemented by the impacted communities. Publications that result from those teaching and learning activities are also included in this thesis and document the intellectual work I've done in graduate school.
Ultimately, using the analytical chemistry skills, developed over my time at University of Maine, I am motivated to make substantial and lasting impacts in the field of water purification.

1.2 Heterogenous catalysis research experiences prior to graduate school

My senior undergraduate research project allowed me to focus more narrowly on the environment. Dr. Austin, a faculty member at Barnard college, was researching lignocellulose-based biofuels as an alternative to fossil fuels and a potential intermediate fuel source for combustion engines and jet fuels. When I signed on to Dr. Rachel Austin’s biofuel project, my social knowledge of the importance of divesting from fossil fuel related energy sources was extensive, but my knowledge of alternative fuels, like low value wood waste typically left on the forest floor, was limited. Such alternatives, I learned, could revitalize rural economies that once depended on wood logging and the pulp and paper industry: Loggers could retrieve the wood waste and the paper mills could be converted to biofuel refineries.

Dr. Austin and her collaborators at the University of Maine had proposed a mechanism for the direct deoxygenation (DDO) of phenol to benzene, consuming only one molecule of hydrogen, over Ru/TiO$_2$. After demonstrating success in the highly selective DDO reaction, two research questions remained. I was able to make valuable contributions to addressing both.

Question 1: Would Ru/TiO$_2$ selectively deoxygenate the aromatic in the presence of a meta or para substituent?

The team came across a study, using Hammett parameters, that looked at the way electronic effects of substituents affected rates. Hammett studies on heterogeneous systems were relatively in their infancy. We selected a catalog of six substituent groups to provide a spectrum of electronic properties and steric effects. Our goal was to run reactions in a high temperature and pressure batch system to produce an initial observation of bond cleavage selectivity. As a result of these explorations, we concluded that to probe the selectivity for C-O bond breakage, we would need to ensure that conversion was reproducible. Unfortunately, the parameters with
which we needed to run those reactions were not sustainable in our laboratory facilities. We held a collaborative team meeting to discuss this limitation. As the only senior on the team, and the only one proficient in using Gaussian software, I was tasked with completing the instructional laboratories. I paired my experiments with the computation calculations to estimate bond dissociation energies to corroborate trends in the experimental data. This allowed me to discuss and demonstrate with our collaborators the principles of Hammett studies and their relevance to understanding mechanistic questions in this more complex system.

Question 2: What is the role of water as a co-catalyst in the DDO mechanism of phenol to benzene?

Prior to my arrival, the team had published the observation that the selectivity for benzene improved from 60% to 95% with 10% water by volume added to the system. Water had an important function in the rate equation for the DDO reaction. To confirm the proposed rate equation, collaborators at the University of Maine ran kinetic isotope effect experiments under deuterium gas and D₂O. We postulated that water was contributing to variable selectivity over multiple types of commercially available titania. I was charged with leading a team of Barnard undergraduates who would incrementally vary the percent of water and report its impact on benzene selectivity over anatase, rutile, p25, and p90. As the team leader, I was responsible for ensuring my team performed in equitable ways that reinforced the data collection and analysis. I had broken down our tasks as experimental, data collection, and data analysis, and created a rotating system to ensure that we were all able to perform all elements of this project. In addition to supporting the students with each of these outlined tasks, I was responsible for synthesizing the ruthenium on the various commercially available titania supports, and image them on the transmission electron microscope. Our collaborators at UMaine ran XPS and BET analysis on these samples that showed sulfur content in the commercially available anatase. I volunteered to perform the synthesis of anatase to eliminate sulfur contamination and to put ruthenium on its surface. To measure the percent ruthenium in all catalysts, we micro digested them and ran
atomic absorption spectroscopy. I compiled and presented our conclusions based on the experiments we ran, and I was able to demonstrate that a 10% by volume water ratio was optimal and that selectivity either plateaued up to 25% or decreased depending on the titania used. I learned many things working on this project, chief of which was the power of collaborative problem solving. Our research findings were published in *Polyhedron* in 2019 under the title *Titania surface chemistry and its influence on supported metal catalysts*. I along with my team members was given co-author credit\(^a\).

During my six months in the Austin lab, I had come to realize that my true passion was chemistry. I was intrigued by my research at the lab and began the process of applying to Chemistry Ph.D. programs that focused on sustainable energy, specifically biofuels and water chemistry. Dr. Austin offered me a twelve-month position as a full-time research assistant working in her lab. I worked closely with a postdoctoral student from the University of Maine on a project that involved using Hammett studies and DFT to model reaction kinetics of substituted benzyl alcohol oxidation over gold on titania.\(^3\) We conducted experiments on substituted benzyl alcohol with various titania supports to see if we could describe the kinetics using a Langmuir Hinshelwood kinetic model and create Hammett slope graphs that would illuminate the electronics of the transition complex in the active site. We had spent the year synthesizing the gold on titania and perfecting these kinetics experiments and the results were published in *ACS Catalysis* in 2020 under the title *Combining Benzyl Alcohol Oxidation Saturation Kinetics and Hammett Studies as Mechanistic Tools for Examining Supported Metal Catalysts*. I had contributed significantly to these experiments and was listed as co-author on the publication\(^b\). I learned a


great deal that year about mass transfer limitations, limiting uncertainty, and proper catalyst storage to avoid deactivation.

These research experiences were valuable to my understanding of surface chemistry, reaction kinetics, and catalyst synthesis/characterization techniques. My exposure to research in heterogeneous catalysis facilitated my ability to problem solve throughout my graduate research work and afforded me the confidence to approach this research project.

1.3 References


Chapter 2

**RH-CATALYZED C-F HYDRODEFLUORINATION**

2.1. Introduction

There are a history of synthesized halogenated hydrocarbon compounds whose practical applications as inert stable compounds were outweighed by their negative environmental and public health impacts. As an example, in the late 1920s a chlorofluorocarbon (CFC), a safer, non-toxic, alternative refrigerant, was synthesized and eight years later 8 million new refrigerators using Freon-12 were sold domestically. In the mid-seventies scientists from the University of California showed that CFCs photolytically decomposed when exposed to UV radiation, creating chlorine atoms. By the mid-eighties scientists linked CFC decomposition from UV radiation in the stratosphere to the depletion of ozone and legislature went into effect in the late eighties to ban certain CFCs globally.

Another instance of a synthesized halogenated compound that caused devastating environmental issues was dichlorodiphenyltrichloroethane (DDT) a common pesticide widely used in the 1940s to combat malaria, typhus, and other insect-borne human diseases. However, the environmental impact of DDT’s widespread use was its effect on large bird reproduction. DDT was found in thinned eggshells and caused cracking and reproductive failure. DDT was banned in the early 1970s due to its impact on the environment as persistent pollutants.

Another class of persistent halogenated compounds manufactured in the early 1930s and subsequently banned in the late 1970s were polychlorinated biphenyls (PCBs). PCBs have widespread applications, for example, they were found in microscope oils, electrical insulators, capacitors, used in solvents for ink carriers in carbonless copy paper. This class of chemicals has been banned since the late 1970s, but their prior improper disposal and subsequent leaching into soil and waterways has led to its persistence in the environment globally.

In addition to synthesized chemical contaminants there are persistent halogenated environmental pollutants that are by-products of industrial waste streams. An example of this is
dioxins, a class of chlorinated biphenyls, that formed from chlorine bleaching of paper pulp. In the 1970 pulp and paper companies were unaware of the potential environmental impacts of dioxins on human health and were reported to accumulate in waterways \(^{13}\) downstream of pulp and paper mills.

In recent years, the class of synthesized chemicals, named poly and perfluoroalkyl substances (PFAS) have been branded as the “forever chemicals”. \(^{14}\) PFAS have persisted in the environment for decades \(^{15}\) and have been linked to global environmental accumulation. \(^{16-17}\) The stability of these saturated fluoro-alkyl compounds makes them useful for a variety of applications such as additives in fire-fighting foam, \(^{18}\) flame retardants, solubilizers for the fracking industry. \(^{19}\) The presence of C-F bonds, not often found in nature, lead to their effectiveness as agents for biological systems for applications such as pesticide use. \(^{20}\) They are widely used in consumer products, pesticides, and pharmaceutical precursors. However, these species, found in multiple consumer products, find their way into the environment through landfill disposal. Continual use of PFAS for consumer goods, coupled with their extraordinary stability, have led to their accumulation in surface water, groundwater, air, and soil. Health experts have reported that long-term exposure to PFAS can contribute to illness. \(^{1}\)

The utility of fluorochemicals has fueled a great deal of research on how to synthesize compounds containing C-F bonds, but relatively little research, in comparison, has gone into studying how to break such bonds \(^{6-17}\). Water treatment plants have few tools to remove low concentrations of PFAS, dioxins, fluorinated benzenes, and related halogenated compounds from waste streams. \(^{21}\) The current best practice method is to extract halogenated compounds by trapping them on the surface of granulated activated carbon (GAC). \(^{21}\) While this method is effective at treating water by trapping PFAS and related compounds, this technique still leaves PFAS contaminated GAC. The purpose of this work is to understand the mechanism by which these strong carbon-halogen bonds can be broken, using a supported noble metal on metal oxide catalyst.
2.1.1. Organic phase de-halogenation chemistry

A number of studies have shown that C-X aromatic bond scission (where -X represents a halide) occurs over Pd, Pt, Ru, Rh, and Ni in the organic phase. These studies give insight into the effect of the choice of metal on the kinetics and trends in the bond strength of carbon-halide bonds in aromatic species. Although carrying out reactions in organic solvents is not directly applicable to environmental PFAS treatment or remediation in the aqueous phase, mechanisms for fundamental dehalogenation chemistry in the organic phase have been hypothesized in the literature and are instructive for development of aqueous-phase chemistry. We survey a number of reports that demonstrate C-X bond breaking over metal catalysts.

Ukisu et al. conducted dechlorination reactions in the liquid phase with 5% noble metal nanoparticles (Rh, Pd, Pt, and Ru) supported on carbon, using 2-propanol as the solvent, and sodium hydroxide that reacts with the HCl produced. Sodium hydroxide, in excess molar amount, was necessary to neutralize the product, HCl, and achieve complete hydrodechlorination at temperatures below 82°C. The process of C-Cl bond breakage in the absence of NaOH is thermodynamically unfavorable. However, the introduction of NaOH created a thermodynamically favorable consumption of HCl, influencing the thermodynamics to lower the enthalpy of C-Cl bond breakage of the chlorobenzene. Chlorobenzene concentration and acetone production were monitored by GC-FID. Reported reaction times of dechlorination of 1,2,4-trichlorobenzene for 5% Rh were fifteen times shorter than 5% Pd/Pt/Ru (see Table 2.1) suggesting that Rh may be a much more active catalyst.
Table 2.1. Efficiency of hydrogen transfer during catalytic dechlorination of 1,2,4-trichlorobenzene in 2-propanol solution. Reproduced from Ukisu et al.23

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction time (h)</th>
<th>Released Cl (mmol)</th>
<th>Produced acetone (mmol)</th>
<th>H-transfer b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Rh/C</td>
<td>0.2</td>
<td>3.5</td>
<td>5.6</td>
<td>63</td>
</tr>
<tr>
<td>5% Pd/C</td>
<td>3.0</td>
<td>2.8</td>
<td>9.5</td>
<td>29</td>
</tr>
<tr>
<td>5% Pt/C</td>
<td>3.0</td>
<td>1.8</td>
<td>9.7</td>
<td>19</td>
</tr>
<tr>
<td>5% Ru/C</td>
<td>3.0</td>
<td>0</td>
<td>2.7</td>
<td>0</td>
</tr>
</tbody>
</table>

a Reaction conditions: 2-propanol, 60 ml; 1,2,4-trichlorobenzene, 1.2 mmol; NaOH, 5.4 mmol; Temperature, 55°C; catalyst, 150 mg.
b 100 × (released Cl)/(produced acetone).

This study suggested a critical role of the solvent in the reaction pathway. Ukisu et al.23 hypothesized that the key step in the dehalogenation of aromatic halides over a noble metal on carbon catalyst was the H-transfer from the solvent, 2-propanol. Conversion of isopropanol to acetone provides hydrogen for the dechlorination reaction. The released Cl was calculated from the change in concentration of chlorobenzene. Percent H-transfer was determined by released chlorine divided by production of acetone. The efficiency of H-transfer was highest for Rh, as illustrated in Table 2.1. Interestingly, Rh had such a fast rate of dehalogenation that Ukisu et al.23 studied the kinetics of Pd because its initial rate was slow enough to observe kinetic processes of C-X bond breakage, and it has a higher H transfer percentage than Pt or Ru. The rate of dehalogenation was fastest for iodobenzene and decreased in the order \( \text{C}_6\text{H}_5\text{I} > \text{C}_6\text{H}_5\text{Br} > \text{C}_6\text{H}_5\text{Cl} > \text{C}_6\text{H}_5\text{F} \), which correlates with the C-X bond strength.

Aramendia et al.22 published speculative mechanistic insights into the dehalogenation of halo-aromatics and emphasized the importance of a basic support. The presence of surface basic sites increased catalytic activity by halogen atoms being captured by the base site on the catalyst surface. Halogenated aromatic substrates, fluoro-, chloro-, bromo-, and iodobenzene were reacted with Pd/C using 2-propanol or potassium formate as hydrogen transfer species at 40 °C. Results from the 2-propanol trials reported a dehalogenation rate of \( \text{C}_6\text{H}_5\text{I} > \text{C}_6\text{H}_5\text{Br} > \text{C}_6\text{H}_5\text{Cl} > \text{C}_6\text{H}_5\text{F} \), relating the bond strength, weak to strong, to the rate of reaction, fast to slow. This work
also showed that decreasing the Pd dispersion from 57 to 7% increased the turnover frequency (TOF) by a factor of 20, showing that the activity is higher on larger particles.

Sawama et al.\textsuperscript{25} hypothesized a Pt/C-catalyzed reaction pathway from liquid phase experiments with more complex fluorinated aromatics by using \textsuperscript{1}H NMR and gas chromatography-mass spectrometry to determine de-halogenated product quantities. Fluorinated aromatics (e.g., for example, 4-fluorobiphenyl) were refluxed for 12 hours, with 10\% Pt/C (3 mol \%) between 80-120 °C depending on the solvent and co-solvent used. Brønsted acidic solvents, such as propanol/methanol/butanol/water, served as a H donor and there was a weak base added for the capture of F\textsuperscript{–} ions, to minimize the risk of hydrogen fluoride accumulation. Scheme 2.1 shows (A) that Pt is activated by H\textsubscript{2}, which then forms the active species (B). A single electron is transferred from (B) into fluoroarene (C). The subsequent F\textsuperscript{–} elimination gives a radical intermediate (E) via an anion radical species (D). A second single electron transfer, yielding species (F), followed by hydrogen atom abstraction from the Pt surface or protonation from H\textsubscript{2}O produces the defluorinated product and the Pt(II), which can be reused and re-reduced by isopropyl alcohol.

Scheme 2.1. Reaction pathway hypothesized by Sawama et al.\textsuperscript{25} for the hydro defluorination of fluorinated aromatic compounds.
Notable key findings from this study were that water increased the rate of dehalogenation, the fluorinated biphenyl had the fastest dehalogenation reactivity followed by Cl > Br >> I, which contrasts with the expected dependence on C-X bond strength. Hydrogenolysis of halo-arenes using the Pt/C-iPrOH/H₂O-Na₂CO₃ combination was not affected by steric hindrance, which would be expected in nucleophilic aromatic substitution and oxidative addition pathways. They suggest an electron-transfer-mediated mechanism where the rate scales with the electronegativity of the halogenated species.

Lu et al.³² report complete defluorination achieved under moderate temperature conditions over Rh, Pd, and a bi-metallic rhodium-indium (Rh-In) complex, see Scheme 2.2. This four-step process begins with hydrogen adsorbed onto the Rh metal, as a hydride species in the presence of tert-butoxide irreversibly creating a Rh(t)hydride/H₂ adduct. Deprotonation of the bound H₂ by tert-butoxide forms a transient Rh(I) dihydride, which relaxes to the Rh¹H₂ adduct. Loss of H₂ adduct generates an unsaturated reactive Rh⁻¹ species 3. Step 3 is the oxidative cleavage of the C-F bond in fluorobenzene. Finally, species 4 reacts with H₂ to produce benzene and the recovered Rh-In complex, 2, ready to enter the catalytic cycle. Lu et al.³² measured all intermediate species in the catalytic cycle through isolation or in situ analysis. While these breakthroughs are significant the application is expensive because they rely on precious metals. Moreover, these catalysts are unable to be applied to the aqueous environment where fluorinated contaminants exist.
Scheme 2.2. Mechanism of defluorination of fluorobenzene over a Rh-In ligand complex. Reproduced from Lu et al.

2.1.2. Aqueous phase dehalogenation chemistry

Only a few studies have reported dehalogenation of halogenated benzenes under aqueous conditions. Notable work on catalytic defluorination chemistry is reported in a series of two papers by McNeill et al. McNeill et al. showed that hydrodefluorination can occur in the aqueous phase at room temperature, using only 1 atm of hydrogen, 5% Rh/Al₂O₃ catalyst and fluorobenzene/phosphate buffer solution. In their initial work, they proposed a reaction network where fluorobenzene is converted rapidly to benzene, followed by hydrogenation to cyclohexane. They showed that C-F bond cleavage was not observed for several possible intermediates, including fluorocyclohexadiene, 3-fluorocyclohexene, and fluorocyclohexane. Isotope labeling studies also indicated that partial hydrogenation did not occur before C-F bond breaking. The hydrogenation of benzene and cyclohexadiene was confirmed to proceed rapidly. Isotope labeling studies in which benzene, cyclohexene, or fluorobenzene were reacted in a D₂/H₂O system showed on average addition of only 1, 1.5 and 1.9 deuteriums, respectively. The low addition rate of deuterium indicates that majority of the hydrogen added to the ring came from water. Although H₂/D₂ exchange experiments provide evidence that H/D exchange occurs on the
Rh catalyst and therefore hydrogenation is reversible. Thus, McNeill et al.\textsuperscript{14} highlight the presence of the aqueous solvent as being critical to achieving hydrogenation under mild conditions.

From the reported kinetics data, McNeill et al.\textsuperscript{29} concluded in their subsequent 2013 paper that the rate-controlling step of the hydrodefluorination (HDF) of fluorinated benzene is the adsorption of the substrate onto the catalyst surface. They concluded that the initial adsorption of fluorobenzene to the catalyst surface is irreversible. This surface adsorption creates an unknown intermediate, I, presumably an adsorbed species. Subsequent C-F bond scission leads rapidly to benzene, and at longer reaction times hydrogenation to cyclohexane in the presence of hydrogen occurs (see Figure 2.1).

Figure 2.1. Proposed reaction pathway of defluorination and hydrogenation of fluorobenzene adapted from McNeill et al.\textsuperscript{29}.

Rate constants for HDF of substituted benzenes, over a 5\% Rh/Al\textsubscript{2}O\textsubscript{3} catalyst are reported in Table 2.2. In this work, the concentration-vs-time data, for the substrate hexafluorobenzene, were fit to an exponential decay, indicating the reaction follows pseudo-first-order kinetics and can be described by a first-order rate law (see Figure 2.2). McNeill et al. reported that all other substituted halogenated benzenes, were fit to an exponential decay indicating pseudo-first-order reaction kinetics. The observed rate constants for defluorination and dechlorination of fluoro- and chlorobenzene are identical within experimental uncertainty, which supported McNeill’s hypothesis that adsorption of the substrate to the surface was rate controlling. That is, if C-X bond breakage was rate-determining, the rate of C-F bond cleavage should be significantly slower than the cleavage rate for other substituted halogenated benzenes because C-F bonds are stronger.
than C-Cl bonds. Since there was no significant difference in the rates of defluorination and
dechlorination it was hypothesized that the adsorption of the substrate to the surface would be
the rate-determining step.

Table 2.2. Pseudo-First-Order Rate Constants ($k_{obs}$), Rate Constants Normalized to the Reactive Standard
($k_{rel}$), Rate Constants Normalized to the Reactive Standard and to the Respective Monohalogenated
Benzene ($k_{rel,norm}$), and Half-lives ($t_{1/2}$, based on $k_{obs}$) for all tested substances. Selected values from McNeill
et al.\textsuperscript{29}

<table>
<thead>
<tr>
<th></th>
<th>Rh: 1.89 mBFe L$^{-1}$</th>
<th>IS: $\alpha,\alpha,\alpha$-trifluorotoluene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{obs}$ (hr$^{-1}$)</td>
<td>$k_{rel}$ ($)</td>
</tr>
<tr>
<td>fluorobenzene (FB)</td>
<td>3.7 ± 0.8</td>
<td>2.7 ± 0.3</td>
</tr>
<tr>
<td>chlorobenzene (CB)</td>
<td>3.0 ± 0.7</td>
<td>1.2 ± 0.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>IS: 4-chlorotoluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluorobenzene (FB)</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>chlorobenzene (CB)</td>
<td>4.7 ± 1.0</td>
</tr>
</tbody>
</table>
Recently Yuan et al.\textsuperscript{27} investigated the hydrodefluorination of fluorophenols using Pd nanoparticles and Pd@Rh core shell and nanowires under aqueous conditions. In this research authors measured the binding strength of dissociated hydrogen adatoms and determined that hydrogen adatoms could poison active sites on the metallic Rh. However, when the particle size was small enough, less than 3 nm, poisoning was not observed. The authors reported advancements for the remediation of contaminated wastewater, by creating catalysts (Pd@Rh nanowires and Pd@Rh/Al\(_2\)O\(_3\)) showing promising applications in HDF of halogentated fluorobenzenes and PFOA.

McNeill’s hypothesis that adsorption is rate-determining was an interesting hypothesis to probe and motivates much of the work in this thesis because usually the rate of reactions is typically governed by the rate of a bond forming or breaking step on the surface. This work aims to explore the reaction kinetics of C-F hydrogenolysis of fluorobenzene catalyzed by a Rh/Al\(_2\)O\(_3\) catalyst. The goal of this thesis is to confirm the reactivity of Rh/Al\(_2\)O\(_3\) under the mild conditions employed by McNeill, et al.,\textsuperscript{29} and to distinguish between an adsorption limited and surface
reaction controlled process. For the research presented in this thesis, the kinetics of C-F hydrogenolysis is measured using a similar experimental set-up to that described by McNeill et al.\textsuperscript{29} From these kinetics measurements, we measured the initial rate of defluorination, from the production of benzene, and elucidated the dependence of the initial rates on the initial concentration of fluorobenzene. Potential rate equations that are consistent with these kinetics data are proposed assuming either 1) an irreversible adsorption step that is rate-determining or 2) a reversible adsorption step followed by a rate-determining C-X bond-breaking step. We then use the full experimental data set to eliminate mechanisms that are inconsistent with the kinetics data.

2.1.3. Theoretical background of reaction kinetics

The conversion of fluorobenzene (FB) to benzene can be written out in five elementary steps. We hypothesize the following set of elementary reaction steps where (*) is defined as a catalyst active site.

1. \( C_6H_5F + * \leftrightarrow C_6H_5F * \)
2. \( H_2 + 2 * \leftrightarrow 2 H * \)
3. \( C_6H_5F * + H * \leftrightarrow C_6H_5 * + HF * \)
4. \( C_6H_5 * + H * \leftrightarrow C_6H_6 * \)
5. \( C_6H_6 * \leftrightarrow * + C_6H_6 \)
6. \( HF * \leftrightarrow HF \)

In step 1, FB adsorbs onto the catalyst surface. In step 2, hydrogen adsorbs dissociatively on the catalyst surface. In step 3, an adsorbed FB and adsorbed hydrogen react, cleaving the carbon-fluorine bond, creating an adsorbed phenyl species and HF. In step 4, a second adsorbed hydrogen will react with the phenyl to form benzene. Finally, benzene and HF will desorb from the surface and be released into the bulk phase.

The elementary steps define a set of coupled differential equations which can, in principle, be solved simultaneously from any initial condition, given values for rate constants and/or equilibrium constants. Frequently, one step is slower than the others and approximate
expressions for the rate law can be derived. As given by Hill and Root, the approach of Hougan and Watson assumes that the reaction involves at least one chemisorbed species and if two species react on the surface, they must be adsorbed on neighboring sites. Therefore, the probability of reaction is proportional to the product of the fractional coverages, $\theta_i$, of species $i$. In contrast, if only one surface species is adsorbed and reacts with a gas phase species, the resulting expression describes an Eley-Rideal type of mechanism. When the reaction only involves surface adsorbed species, the reaction is considered a Langmuir-Hinshelwood type of mechanism. When the coverage of $\theta_i$ is assumed to obey the Langmuir isotherm, a Langmuir-Hinshelwood-Hougan-Watson (LHHW) rate expression is obtained.

In addition to the assumptions of the Langmuirian adsorption, two limiting cases can be considered: 1) Adsorption equilibrium is maintained for all species and the overall rate of the reaction is given by the rate of chemical reaction on the surface; and 2) the rate of the surface chemical reaction is sufficiently fast that adsorption equilibrium is not achieved, but the steady state approximation is valid and therefore the coverage of the species that is not in adsorption equilibrium remains constant at a value below its equilibrium value. For the second case, the reaction may be adsorption or desorption limited.

We first derive the general case in which the surface reaction (step 3) is rate-limiting (Case 1) and all species are in equilibrium. The rate of the surface reaction,

$$ r = \theta_{FB} \theta_H. $$

(1)

where $\theta_{FB}$ is the coverage of fluorobenzene and $\theta_H$ is the coverage of hydrogen atoms. If all species compete for the same adsorption sites, expressions for the coverage of each reactant species are given by the Langmuir isotherm as,

$$ \theta_H = \frac{\sqrt{K_{H2}P_{H2}}}{1 + K_{FB}P_{FB} + \sqrt{K_{H2}P_{H2}} + K_B P_B + K_{HF}P_{HF}}, $$

and

$$ \theta_{FB} = \frac{K_{FB}P_{FB}}{1 + K_{FB}P_{FB} + \sqrt{K_{H2}P_{H2}} + K_B P_B + K_{HF}P_{HF}}. $$

(3)

Where the equilibrium constant for species $I$,
\[ K_i = \frac{k_{\text{ads}}}{k_{\text{des}}} \]  

is related to the adsorption and desorption rate constants, \( k_{\text{ads}} \) and \( k_{\text{des}} \), respectively. The general case includes the coverage of benzene, \( B \), and hydrogen fluoride, \( HF \). The overall rate is then given by

\[ r = \frac{K_{FB}P_{FB}\sqrt{K_{H2}P_{H2}}}{(1+K_{FB}P_{FB}+\sqrt{K_{H2}P_{H2}+K_{B}P_{B}+K_{HF}P_{HF}})^2}. \]  

Species that accumulate on the surface are called abundant surface intermediates and appear in the denominator, which are known as the site-blocking term(s). Frequently, only one or two species have significant coverage and are referred to the most abundant surface intermediate (MASI) species. With an assumption that the coverage of one of the species is larger than the other species, the denominator retains only the related term. As an example, if fluorobenzene (FB) is the MASI, then

\[ r \approx \frac{K_{FB}P_{FB}\sqrt{K_{H2}P_{H2}}}{(1+K_{FB}P_{FB})^2}. \]  

is the LHHW rate expression for the surface limited reaction.

We next consider the case where the reaction is adsorption limited with only fluorobenzene not in adsorption equilibrium and the surface reaction is reversible. Therefore, for step 3, at steady state

\[ k_3 \theta_H \theta_{FB} = k_{-3} \theta_B \theta_{HF}, \]  

and therefore, the steady state coverage of FB is

\[ \theta_{FB} = \frac{k_{-3} \theta_B \theta_{HF}}{k_3 \theta_H} = \frac{\theta_B \theta_{HF}}{K_3 \theta_H}. \]  

Combining \( \theta_{FB} \) with the Langmuir expressions for all other species, the site balance is given by

\[ 1 = \frac{K_{B}P_{B}K_{HF}P_{HF}}{K_3\sqrt{K_{H2}P_{H2}}\theta_V + \sqrt{K_{H2}P_{H2}}\theta_V + K_{B}P_{B}\theta_V + K_{HF}P_{HF}\theta_V + \theta_V}. \]
The coverage of vacant sites is

$$\theta_V = \frac{1}{1 + \frac{K_{BF}P_{BF}K_{HF}P_{HF}}{K_3/K_H^2P_{H2}^2 + \sqrt{K_{H2}P_{H2} + K_BP_B + K_{HF}P_{HF}}} + \sqrt{K_{H2}P_{H2} + K_BP_B + K_{HF}P_{HF}}}$$

(10)

Because the rate of the overall reaction is the rate of adsorption of FB, the net rate of the reaction is the difference between the rates of adsorption and desorption,

$$r = k_{ads}^{FB} P_{FB} \theta_V - k_{des}^{FB} \theta_{FB}.$$  

(11)

This leads to the adsorption limited rate expression,

$$r = k_{ads}^{FB} \left( P_{FB} - \frac{K_{BF}P_{BF}K_{HF}P_{HF}}{1 + \frac{K_{BF}P_{BF}K_{HF}P_{HF}}{K_3/K_H^2P_{H2}^2 + \sqrt{K_{H2}P_{H2} + K_BP_B + K_{HF}P_{HF}}} + \sqrt{K_{H2}P_{H2} + K_BP_B + K_{HF}P_{HF}} + \sqrt{K_{H2}P_{H2} + K_BP_B + K_{HF}P_{HF}}} \right).$$

(12)

2.2. Methods

2.2.1. Materials

5% Rh/Al₂O₃ was purchased from Sigma Aldrich (Product No. 212857-5G. Lot MKCM3442). Alumina (γ-Al₂O₃) was purchased from Fisher Scientific (CAS No. 1344-28-1 Lot 995363) Fluorobenzene 99% (CAS No. 462-06-6) was purchased from Sigma Aldrich. Methylene chloride (99.5%) was purchased from Fisher Scientific. All materials were used as received. A Fischerbrand Isotemp Advanced Stirring Hotplate was purchased from Fischer Scientific. Triangular stir bars were purchased from the lab depot. 8 mL glass vials were purchased from Chem Glass Life Sciences. 150 µL glass inserts (5183-288, Agilent) for GC-MS vials and PFTE screw caps (5182-0717, Agilent) were purchased from Fischer Scientific. 20 mm rubber septa were purchased from Fischer Scientific. A 500 µL Hamilton glass fixed needle syringe was purchased from Sigma Aldrich.
2.2.2. Instrument specifications

2.2.2.1. Gas chromatography mass spectrometry method development

The analytical instrument used was a 7820A gas chromatograph-mass spectrometer (GC-MS), with a 5977E network mass selective detector, manufactured by Agilent Technologies. The inert gas used was UHP He; separation was achieved using a 5% phenyl methyl polysiloxane column [30 m x 250 µM x 0.25 µM] (HP-5, 19091J-433, Agilent). A 7963 series autoinjector was used to allow for multiple samples to be run overnight.

All samples were run on an optimized method, the parameters of which are as follows: inlet temperature was 275 ºC, operating pressure was 8.5 psi, with a total flow of 1.2 mL/min. To preserve the small amount of available sample, no pre-injection rinses were included, but the sample was washed 5 times in the syringe before injecting 1µL of total sample into the instrument. The syringe was rinsed 3 times with methylene chloride after each sample injection. A solvent delay of 2.5 min was used to minimize the solvent peak since it had the potential to obscure the product peak benzene at 2.7 min and to shorten the filament life.

The oven setpoint was 30 ºC and was held constant for 8.5 min. The temperature was ramped at a rate of 25 ºC/min until the temperature of the oven reached 270 ºC. The total method run time was 15.6 min.

The instrument method used a gain factor of 25. Samples were run with a split ratio of 5:1, which further decreased the amount of material injected onto the instrument to avoid over saturating the column with fluorobenzene, which would accumulate on the instrument column leading to skewed peaks intensities over time.

2.2.2.2. Gas chromatography mass spectrometry calibration standards

Calibration curves of fluorobenzene and benzene were generated to quantify the relationship between the GC-MS area under the curve (AUC) and the concentration of the substrate, fluorobenzene, and product, benzene. Standard 200 µM solutions of fluorobenzene
and benzene were made in volumetric glassware separately using phosphate buffered saline, 150 mM NaCl and pH= 7.4. The stock solutions were diluted in 4 mL conical vials to achieve concentrations of 5, 10, 20, 30, 50, 70, 100 µM for benzene and 10, 20, 30, 50, 70, 100 µM for fluorobenzene. In separate 1 mL centrifuge tubes, the substrate was extracted into methylene chloride with the following aliquots of substrate:methylene chloride: dilution 1:2 (100 µL:50 µL), concentrated 4:1 (50 µL:200 µL), and concentrated 2:1 (50 µL:100 µL). The biphasic samples in the centrifuge tubes were vortexed for 40 s and centrifuged for 5 min before approximately 30 µL of the organic layer was placed in a glass insert into a GC-MS vial to be analyzed via GC-MS. The calibration standards were made to reflect the starting concentrations of fluorobenzene and the expected range of benzene concentrations after extraction with methylene chloride shown in Figure 2.3. The calibration data in Figure 2.3 were produced by extracting the standard solutions into methylene chloride using the 1:2, 4:1, and 2:1 ratios and then dividing the AUC by the concentration ratio. In addition, the instrumental limits of detection vs quantification were established based on the ion abundance measured by MS reporting values with a magnitude equal to or greater than $10^4$ and the peak shape in the chromatogram. The limit of detection was more rigorously calculated as the ratio of the standard deviation of the curve multiplied by the numerical constant, 3.3, and divided by the slope. Based on this quantitative tool, the limits of detection were determined to be 0.1 µM for fluorobenzene and 0.3 µM for benzene. The limits of quantification were 0.3 µM for fluorobenzene and 1 µM for benzene.
Figure 2.3. Calibration curves for A) fluorobenzene and B) benzene standard solutions extracted in methylene chloride. AUC has been divided by the concentration factor.

2.2.2.3. Gas chromatography mass spectrometry extraction efficiencies

Our reaction takes place in the aqueous phase and as a result, analytical methods were limiting as both GC-MS and GC-FID require an organic solvent. To circumvent this limitation, reaction solutions were concentrated in methylene chloride, an organic solvent more dense than water. This density difference with respect to water resulted in clear phase separation with the desired product separating into the smaller portion of the centrifuge tubes used to collect sample fractions. In addition, this immiscible mixture was easy to vortex and centrifuge, allowing separation of the aqueous and organic layers.

Figure 2.4 shows the extraction efficiency of fluorobenzene and benzene in methylene chloride. In this figure, the blue circles represent the AUCs extracted in methylene chloride using the same procedure described above and the orange circles represent solutions of benzene (10 μM, 30 μM, and 200 μM) and FB (10 μM, 30 μM, and 250 μM) made directly in methylene chloride. The extraction efficiency of FB and benzene are 75% and 38%, respectively, calculated by taking the ratio of the slope of the extracted compounds to the slope of the direct calibration solution.
Figure 2.4. Calibration curves for standard solutions extracted in methylene chloride and standards made with methylene chloride as a solvent for A) fluorobenzene and B) benzene.

In the data analysis, the slope of the extracted calibration solutions was used because the concentrations of benzene being produced were between 5 µM-15 µM. Based on a comparison of the slopes of the calibration curves, the extraction efficiency was approximately 40%. The FB concentrations after extraction were not used for analyzing the kinetics of C-F bond breakage because the change in concentration over time was lower than 10% of the initial FB concentration and it was difficult to accurately use those differences to determine the kinetics of C-F bond breaking. In addition, from Figure 2.4A, the efficiency of extraction decreases as the initial FB concentrations increase leading to difficulties analyzing the true conversion factor of AUC to concentration.

2.2.2.4. High-resolution transmission electron microscopy

High-resolution transmission electron microscopy (HR-TEM) analysis was performed at Columbia University Nanoinitiative (CNI) electron microscopy facilities using an FEI Talos F200X transmission/scanning transmission electron microscope. The analyzed catalysts were mixed with a minimal amount of 2-propanol, and the mixture was suspended on a lacey carbon film on a Cu grid or a silicon nitride membrane grid with a membrane thickness of 50 nm, frame thickness of 50 mm and nine 0.1 mm windows. The operating voltage of the FEI Talos was 200 kV.
Micromeritics physisorption and chemisorption experiments

Nitrogen physisorption isotherms on 5% Rh/Al₂O₃ and γ-Al₂O₃ were performed separately on an ASAP 2020 accelerated surface area and porosimetry system manufactured by Micromeritics. The degas and analysis procedures were identical for both samples. For each, roughly 100 mg of sample was massed into a clean/dried tube. The procedure for the evacuation phase started with the sample degassing, where all impurities were removed from the surface and the pores by pumping down the sample and raising the temperature. The degas program began with a temperature ramp rate of 10 °C/min, target temperature of 90 °C, evacuation rate of 10 mmHg/s, vacuum setpoint of 40 mmHg, and evacuation time of 60 min. The heating phase had a setpoint of 350 °C, ramp rate of 10 °C/min, and a hold time of 240 min under a turbomolecular pump vacuum of <10⁻⁶ torr. After the sample was degassed, the sample was backfilled with He and put onto the analysis port where the He was removed from the sample tube. The warm free space was measured by expanding He from the manifold into the sample tube and measuring the pressure decrease. Subsequently, the sample tube was submerged into a liquid nitrogen dewar and the cold free space was measured from the further decrease in pressure after the sample was cooled to 77 K. The saturation pressure, P₀, was measured as the nitrogen pressure in equilibrium with liquid phase N₂ in the dip tube submerged in the liquid nitrogen dewar. The sample analysis began with filling nitrogen in the manifold and measuring the pressure while it is sealed off from the sample tube. Once the pressure stabilized the valve to the sample tube is opened, allowed to equilibrate, and nitrogen physisorbs on the catalyst surface. The difference between the pressure in the manifold and the pressure expected based on expansion into the cold free space is used to calculate how much nitrogen was physisorbed. This dosing continues and builds up multiple layers of nitrogen on the catalyst surface. To begin the desorption process, the pressure is lowered in the isolated manifold, and then the valve to the sample tube is opened, allowed to equilibrate, and nitrogen that desorbs is measured by difference again.
Chemisorption was performed on an ASAP 2020 chemi accelerated surface area and porosimetry system manufactured by Micromeritics. Chemisorption is an interaction where electrons are shared between the gas molecule and the solid surface. Chemisorption is selective and will only adsorb in a monolayer on the metallic active sites on a catalyst surface. Therefore, they can only chemically bond with surface sites.

Hydrogen chemisorption was conducted on the 5% Rh/Al₂O₃ catalyst in which a sample of roughly 80 mg was added into a cell between two plugs of glass wool. After the cell was evacuated from any impurities in the cell and on the surface of the catalyst, the sample was heated in the presence of hydrogen at 250 ºC for 30 min, cooled down to 35 ºC and evacuated again. Helium was used to measure the warm free space of the cell and evacuated. The first isotherm was collected by holding the cell at 35 ºC, as hydrogen was dosed into the cell incrementally up to 500 Torr. The measured hydrogen pressure was used to calculate the hydrogen uptake as the difference in pressure between the dosed cell and the pressure expected based on the warm free space. After evacuation of the sample, a second isotherm was measured. The difference between the first and second adsorption isotherms yields the chemisorption isotherm which identifies the particle dispersion of the metal oxide catalyst. The dispersion was calculated from the micromoles of sites divided by the Rh metal loading, where it was assumed that there are 2 sites per adsorbed hydrogen atom.³⁴

2.2.3. Batch reactor experiments

In an 8 mL conical vial, approximately 5.00 g of fluorobenzene solution in 1xPBS (10 mM, pH= 7.4) and 0.6 to 0.8 mg of 5% Rh/Al₂O₃ diluted in γ-Al₂O₃ (1:10 dilution) were mixed. The NaCl concentration in the buffer solution was measured by ion chromatography to be 150 mM. In this reaction, PBS converts bulk phase HF₉(g) into aqueous fluoride for safety. With respect to safety, a separate waste container was used for these experiments to prevent mixing of fluorinated compounds with other wastes generated in the laboratory.
The mixture was stirred at 1470 rpm with a conical stir bar. The stock solution of fluorobenzene in 1xPBS was sonicated for 5 min and inverted 40 times before each experimental trial. The solution and catalyst were stirred for 10 min. in the absence of hydrogen. While the mixture was stirring, 30 psi of hydrogen was pressurized into an emptied hydrogen purged 25 mL Parr reactor vessel using a 4848 series Parr Instruments reactor controller (Figure 2.5). At the outlet, a rubber tube fitted with a septum was punctured with a hypodermic needle at the end of a hydrogen balloon. After the solution in the glass vial was stirring for 10 min, the headspace was purged with 30 psi of hydrogen gas, thereby starting the reaction, until the balloon deflated (approximately 15 s). A second hydrogen balloon with 30-40 psi was immediately inserted into the headspace (Figure 2.5). 100 µL of the reaction solution was sampled at multiple time points using a 500 µL glass syringe and was concentrated in 50 µL of methylene chloride. The biphasic solution was vortexed for 40 s and then centrifuged for 5 min in a plastic 1.5 mL centrifuge tube. The bottom organic layer of methylene chloride containing substrate and product of interest was extracted into a 150 µL glass insert for gas chromatography vials. The extracted organic layer was then analyzed via GC-MS.
2.2.4. Control experiments

In an 8 mL conical vial, 5.00 g of fluorobenzene solution was run in pure $\gamma$-$\text{Al}_2\text{O}_3$ analogous to the batch reactor experimental method detailed in the section above. Reaction sampling was done at 15, 30, 60, 90 min. The GC-MS chromatograms showed fluorobenzene concentration fluctuates as fluorobenzene adsorbs and desorbs to the surface of the $\gamma$-$\text{Al}_2\text{O}_3$. However, no apparent benzene generation occurred over 90 min.

A second control experiment was run in an 8 mL conical vial, 5.00 g of fluorobenzene solution was run in the (1:10) physical mixture of 5% Rh/$\text{Al}_2\text{O}_3$: $\gamma$-$\text{Al}_2\text{O}_3$ in the absence of $\text{H}_2$. Reaction sampling was done at 15, 30, 60, 90 min. The GC-MS chromatograms showed, similarly, that fluorobenzene concentration fluctuates as fluorobenzene adsorbs and desorbs to the surface of the $\gamma$-$\text{Al}_2\text{O}_3$. There was no benzene present in the chromatogram over 90 min.
2.2.5. Major takeaways from experimental method development

When testing the reproducibility of the kinetics measurements there were initially a few modifications to the ways in which we were preparing and taking proper precautions to create consistent fluorobenzene solutions, namely:

- FB stock solutions in PBS were sonicated for 10 min before the 5.00 g aliquot was massed into the reaction vial; and.

- At the lowest FB concentration, even after sonicating, we speculate that in the low concentration regime, <100 μM, FB could adhere to glass, so we made fresh FB stock solutions for each experimental trial and sonicated each for 15 min immediately prior to use.

FB solubility in water has been cited\textsuperscript{35} and discussion in the literature about possible fluoros-phase aqueous chemistry at ambient temperatures and pressures.\textsuperscript{36-37}

2.2.6. Kinetics data fitting

A MATLAB program was used to solve the batch reactor (CSTR) model for a variety of proposed LHHW rate equations as a function of time for the given initial FB concentration. For each reaction mechanism, the MATLAB program predicted the FB and benzene concentrations and attempted to optimize the kinetic parameters to match the measured values for each of the reaction time points.

Specifically, MATLAB routine was divided into three sections, each defining a function. Function 1 minimizes the error between the experimental data and the model by optimizing the rate constants. The non-linear least squares regression fit function (the built-in ‘nlinfit’ routine) requires as input a time array and the array of concentrations of the reactant and product, as well as initial guess values for the kinetic parameters for the rate equation. The output of Function 1 is the optimal apparent rate and equilibrium constant values. Function 3 defines the rate equation, which uses the global values of the parameters, including the rate and equilibrium constant
variables, and concentration. The output column vector D is used as an input for the ODE solver function. Function 2 calls the ODE solver function to solve the set of ordinary differential equations. Function 2 returns the values of the concentrations at the experimental time points. The MATLAB plotting parameters for the raw data and model function are also defined under Function 2.

2.3. Results and Discussion

2.3.1. Catalyst characterization

Figure 2.6.A-B show the N\textsubscript{2} isotherms for $\gamma$-Al\textsubscript{2}O\textsubscript{3} and 5\% Rh/Al\textsubscript{2}O\textsubscript{3} respectively. Figure 2.6.C shows the BET plot over the range of P/P\textsubscript{0} from 0.05 to 0.25\cite{38}. The BET surface area is defined as the area occupied by the quantity of N\textsubscript{2} adsorbed in a monolayer, calculated from the slope and the intercept of Figure 2.6.C, using a N\textsubscript{2} molecular cross-sectional area of 0.162 nm\textsuperscript{2}. The N\textsubscript{2} BET surface area for $\gamma$-Al\textsubscript{2}O\textsubscript{3} was reported as 184 m\textsuperscript{2}/g. The N\textsubscript{2} BET surface area for 5\% Rh/Al\textsubscript{2}O\textsubscript{3} was reported as 164 m\textsuperscript{2}/g. A C parameter of 91 was reported for $\gamma$-Al\textsubscript{2}O\textsubscript{3} and 122 for 5\% Rh/Al\textsubscript{2}O\textsubscript{3}. The magnitude of the C parameter is characteristic of the strength of the adsorbate (N\textsubscript{2})/surface interactions. A C parameter between 50-150 suggesting that the N\textsubscript{2} is spread smoothly over the surface.

Pore size distributions were calculated using the Barrett, Joyner, and Halenda (BJH) method and are shown in Figure 2.6.D\cite{39}. The average pore diameter of $\gamma$-Al\textsubscript{2}O\textsubscript{3} was 55 Å. The average pore diameter of 5\% Rh/Al\textsubscript{2}O\textsubscript{3} was 101 Å.
Figure 2.6. N₂ BET surface analysis of A) γ-Al₂O₃ (blue circles) and B) 5% Rh/Al₂O₃ (black diamonds), C) BET plot, and D) differential pore size distribution (BJH).

Figure 2.7 shows hydrogen uptake data after volumetric dosing (blue diamond) and after evacuating the non-chemisorbed hydrogen (red square). Hydrogen chemisorption analysis calculated a hydrogen uptake of 70 µmol H₂ per gram catalyst. Based on a H:Rh stoichiometry of 1:1, the corresponding number of surface Rh atoms was 139 µmol Rh per gram catalyst. The dispersion was calculated by surface loading of Rh µmol per gram catalyst divided by total number of Rh atoms per gram of catalyst. Rhodium particle dispersion, D, was calculated to be 28%. The rhodium particle size, d =1.1/D, was 3.8 nm.
Figure 2.7. H₂ chemisorption isotherms. H₂ dosing on the catalyst surface and pressure measurement relative to the hydrogen uptake is represented by the blue diamonds. After evacuation of the dosed H₂, the isotherm is remeasured to see how much H₂ has chemisorbed to the metal sites on the catalyst, as shown in the red squares.

Figure 2.8 shows representative HRTEM images of A) 5% Rh/Al₂O₃ and B) the physical mixture of 1:10, 5% Rh/ Al₂O₃: γ-Al₂O₃. By inspection, the Rh particle size reported is similar to the value estimated from H₂ chemisorption.

Figure 2.8. High-resolution TEM image of A) 5% Rh/Al₂O₃ and B) a 1:10 dilution of 5% Rh/Al₂O₃ to γ-Al₂O₃.
2.3.2. Evaluation of mass transport limitations

Overall reaction rates may be limited by the rate of surface reactions or by mass transport. Mass transport may, in turn, be limited by internal gradients – those gradients confined within particles – to the local reaction zone, or external gradients between the bulk solution and solid phases. To assess the significance of external mass transport we varied experimental stirring speed. In this experiment, the reaction of 320 µM fluorobenzene was stirred at 1470 rpm and 1324 rpm and the calculated rate of benzene production were 0.0048 µM/sec⁻¹mg⁻¹ catalyst regardless of stirring speed. We therefore conclude that the reaction of FB is not limited by external mass transfer, and all FB solutions were subsequently stirred at 1470 rpm.

To assess whether the reaction for FB and H₂ was limited by the rate of internal mass transfer in the liquid phase, the Weisz-Prater (W-P) number \(^{40}\) (a dimensionless quantity that compares the rate of reaction to the rate of mass transfer of reactant to the active sites in pores spaces) was calculated for each substrate using equations (13), (14) and (17). The W-P number offers insight into internal mass transfer diffusion limitation and is determined via readily measured or calculated parameters (see Table 2.3). For this calculation, the catalyst pellet radius, \(R_p\), was qualitatively estimated to be 50 µm from HRTEM images of whole catalyst particles; the observed rate, \(r_{\text{obs}}\), estimated from the maximum rate obtained in the experimental data analysis; the surface concentration, \(C_s\), was estimated for FB to be the largest initial concentration from the experimental data collection, and for H₂ was calculated as the partial pressure of H₂ in the reaction divided by the quantity of the temperature (K) of the reaction and ideal gas constant (cm\(^3\) atm g mol\(^{-1}\) K\(^{-1}\)). Because our reaction takes place in the liquid phase, the bulk diffusivity for H₂ in water and FB in water must be calculated separately using equations (15) and (16) respectively. The mean free path, \(\lambda\), was calculated from the ratio of radius of the substrate molecule found from the NIST database and radius of the catalyst pore determined by BJH analysis of N\(_2\) physisorption data; temperature, \(T\), was set at a typical room temperature of 27-30 ºC; the molecular weight of the solvent, \(M_{\text{H}_2\text{O}}\), was determined from the periodic table of elements. The following values were
obtained from a table of physical constants\textsuperscript{26}, the solvent association parameter, \( \chi \); the fitting parameter, \( P \); the molar volume of component \( i \) at normal boiling point, \( V_i \), the and the viscosity of water, \( \eta \), at 30 °C. The Weisz-Prater criterion is given by

\[
N_{W-P} = \frac{r_{\text{obs}} R_p^2}{D_{\text{eff}} C_s} \ll 0.3
\]  
(13)

\[
D_{\text{eff}} = D_b \frac{(1-\lambda)^2}{1+P\lambda}
\]  
(14)

\[
D_b|_{\text{H}_2 \text{in H}_2 \text{O}} = \frac{1.1718 \times 10^{-16} T \sqrt{V_i M_{\text{H}_2 \text{O}}}}{\eta_{\text{H}_2 \text{O}} V_{\text{H}_2}}
\]  
(15)

\[
D_b|_{\text{FB in H}_2 \text{O}} = \frac{8.621 \times 10^{-14}}{\eta_{\text{H}_2 \text{O}} V_{\text{FB}}}
\]  
(16)

\[
\lambda = \frac{r_{\text{molecule}}}{r_{\text{pore}}}
\]  
(17)

Table 2.3. Weisz-Prater calculation: terms, definitions, and values for equations (13)-(17).

<table>
<thead>
<tr>
<th>Term [units]</th>
<th>Definition of Term</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{\text{obs}} ) [mol cm(^{-3}) s(^{-1})]</td>
<td>the observed rate of reaction</td>
<td>( i = \text{FB} ) 6E-9</td>
</tr>
<tr>
<td>( R_p ) [cm]</td>
<td>radius of catalyst pellet</td>
<td>0.025</td>
</tr>
<tr>
<td>( C_s ) [mol cm(^{-3})]</td>
<td>concentration of substrate at the surface</td>
<td>1.1E-3 8.2E-5</td>
</tr>
<tr>
<td>( D_{\text{eff}} ) [cm(^2) s(^{-1})]</td>
<td>effective diffusivity</td>
<td>5.6E-4 6.1E-4</td>
</tr>
<tr>
<td>( D_b ) [cm(^2) s(^{-1})]</td>
<td>bulk diffusivity</td>
<td>1.2E-3 1.3E-3</td>
</tr>
<tr>
<td>( \lambda ) [dimensionless]</td>
<td>mean free path</td>
<td>0.055 0.053</td>
</tr>
<tr>
<td>( r_{\text{molecule}} ) [cm]</td>
<td>molecular radius of molecule ( i )</td>
<td>1.25E-8 1.2E-8</td>
</tr>
<tr>
<td>( r_{\text{pore}} ) [cm]</td>
<td>radius of the smallest pore (BJH distribution)</td>
<td>2.3E-7</td>
</tr>
<tr>
<td>( P ) [dimensionless]</td>
<td>fitting parameter (ref\textsuperscript{26})</td>
<td>16.26</td>
</tr>
<tr>
<td>( T ) [K]</td>
<td>temperature of the reaction liquid</td>
<td>303.15</td>
</tr>
<tr>
<td>( \chi ) [dimensionless]</td>
<td>solvent association parameter (for H(_2)O ref\textsuperscript{26})</td>
<td>2.6</td>
</tr>
<tr>
<td>( M_{\text{H}_2 \text{O}} ) [g mol(^{-1})]</td>
<td>molecular weight of water</td>
<td>18.01528</td>
</tr>
<tr>
<td>( \eta_{\text{H}_2 \text{O}} ) [Pa s]</td>
<td>viscosity of water</td>
<td>7.972E-4</td>
</tr>
<tr>
<td>( V_i ) [m(^3) kmol(^{-1})]</td>
<td>molar volume of component ( i ) at its normal boiling point</td>
<td>0.0939 0.0284</td>
</tr>
<tr>
<td>( N, W-P_{\text{in H}_2 \text{O}} )</td>
<td>Weisz Prater number for substrate ( i ) in water</td>
<td>6.3E-6 7.5E-5</td>
</tr>
</tbody>
</table>

As calculated for our experimental conditions, the larger value of the W-P number (7.5E-5) for the internal mass transfer limited process by H\(_2\) was significantly less than 0.3. This very low value relative to the threshold of 0.3 indicates that the reactions were also not limited by internal mass transfer.
2.3.3. Adsorption experiments

Because these experiments are being conducted in the liquid phase at room temperature, the substrate is more likely to adsorb on the catalyst surface than typically occurs in gas phase reactions at elevated temperatures. Adsorption experiments were performed to evaluate the extent of adsorption of fluorobenzene and benzene on the 5% Rh/Al₂O₃ diluted 1:10 in γ-Al₂O₃. Figure 2.9 shows the adsorption experiments, performed in separate 8 mL vials, where 5.0 g of stock solutions of 100 µM FB and 250 µM benzene solutions were stirred for 10 min in the absence of H₂ with 0.6 mg of the 1:10 catalyst mixture. Uptake of fluorobenzene and benzene onto the catalyst surface can be calculated as the molar difference between the initial concentrations and equilibrium concentrations. Following this approach, there are 0.5 µmol benzene and 0.15 µmol FB that are calculated to be present on the catalyst surface at the start of the reaction. To calculate the amount of surface Rh, we take the mass of the 5% Rh/Al₂O₃ (0.06 mg) and multiply it by the percent of Rh in the catalyst and the dispersion of surface Rh estimated from H₂ chemisorption experiments. The calculated amount of Rh on the surface of the catalyst is 8.2x10⁻³ µmol. This value is significantly less than calculated uptake, suggesting that fluorobenzene and benzene are saturating the Rh and are also physisorbed on the γ-Al₂O₃ support. Using a weighted average, 90% γ- Al₂O₃ and 10% γ- Al₂O₃ from 5% Rh/Al₂O₃ and multiplying by the mass of catalyst gives an estimate of γ-Al₂O₃ surface area of 0.109 m². From this calculation we can also report the number of molecules per square nanometer, for benzene this value is 2 molecules/nm² γ-Al₂O₃ and for FB is 1 molecules/nm² γ-Al₂O₃.
Figure 2.9. Adsorption of benzene and fluorobenzene with a 5% Rh/Al₂O₃ catalyst diluted (1:10) in γ-Al₂O₃ stirred in the absence of H₂. Experiments with each substrate were performed separately.

The catalyst was stirred in a mixture of fluorobenzene, and 1xPBS in the absence of hydrogen for 10 min. As a result of this pre-reaction step, fluorobenzene was adsorbed on the metal catalyst as well as the inert γ-Al₂O₃ support. This initial condition is different from the conditions used by McNeill et al.,²⁸ who began their reactions by introducing the catalyst suspended in pure phosphate buffer via syringe into a round bottom flask which already contained fluorobenzene, phosphate buffer solution, and hydrogen gas. Differently than McNeill, experiments reported in this work began with a fluorobenzene saturated catalyst surface and introduced hydrogen last.

2.3.4. Rate of benzene production over two concentration regimes

Reaction rates of hydrodefluorination were quantified by measuring the production of benzene as a function of time over a FB concentration ranging from 85 µM to 1.065 mM. In this experimental set-up, FB is selectively converted to benzene. The relationship between the concentration of benzene and time for initial fluorobenzene concentrations below 450 µM is shown
in Figure 2.10A. Initial defluorination rates increase with the concentration of fluorobenzene as shown by the slopes of the linear fits in Figure 2.10A. The concentration vs time data for initial FB concentrations above 450 µM is shown in Figure 10B, where, at low conversion (<10%) the data no longer shows a linear relationship between concentration and time, suggesting a rate that accelerates as a function of time.

Figure 2.10. Average benzene concentration, representing an average of three replicates, as a function of time at initial fluorobenzene concentrations A) below 450 µM and B) above 450 µM. Error bars represent the standard deviations from the three reaction trials.

The goal in these types of kinetic experiments is to make measurements in the initial stages of the reaction where the “initial rate” that can easily be measured i.e., it approximates the instantaneous rate. Typically, as reactants disappear, the rate slows as a function of the form of the rate equation. Thus, it is important to capture the initial increase in benzene concentration as a function of time. To estimate these initial rates, data points were selected from the linear regime. A plot of the calculated slopes from the linear regimes versus the initial FB concentration is shown
in Figure 2.11. The rate generally follows a LHHW form, appearing first-order at low FB concentrations and near zero-order at high FB concentrations.

![Graph showing initial rates of benzene production as a function of initial fluorobenzene concentrations](image)

**Figure 2.11.** Initial rates of benzene production as a function of the initial fluorobenzene concentrations using data points from the linear regime of [benzene] versus time. Error bars represent the 95% confidence interval of the linear weighted least squares fit of [benzene] versus time plots.

2.3.5. Potential reaction sequences

We first evaluated several rate laws based on the elementary reaction steps given in section 2.1.4 in the surface reaction limited case and determined whether they are consistent with the initial rate data in Figure 2.11. Each model uses the set of elementary reaction steps outlined above, with the rate determining step and MASI species as defined in Table 2.4. Rate equations are derived from the set of elementary reactions steps preceding/including the rate determining step. Quasi-equilibrated elementary reaction steps are described by an equilibrium constant,
which is the concentration of the product species divided by the concentration of reactant species in that step. The sum of the coverages of the most abundant surface intermediate (MASI) and vacant sites is set equal to one. MASI species were selected based on the surface species preceding the rate-determining step (RDS) and appears in the denominator of the overall rate equation as a site blocking term. As the species increases in surface abundance, it will block active sites on the surface leading to an overall decrease in reaction rate. Detailed derivations of the rate equations are in the Appendix (A.1).
Table 2.4. Elementary reaction steps, where (*) represents an active site on the surface of the catalyst.

From the elementary reaction steps, the rate equations were derived, and the most abundant surface intermediate(s) (MASI) were assigned to four distinct models.

<table>
<thead>
<tr>
<th>Elementary Reaction Steps</th>
<th>Derived Rate Equation</th>
<th>MASI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model 1A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. C₆H₅F + * ↔ C₆H₅F*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>2. H₂ + 2 * ↔ 2 H*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>3. C₆H₅F + H* ↔ C₆H₆* + HF*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>4. C₆H₅* + H* ↔ C₆H₆*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>5. C₆H₆* + * ↔ + C₆H₆</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>6. HF * ↔ HF</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td><strong>Model 1B</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. C₆H₅F + * ↔ C₆H₅F*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>2. H₂ + 2 * ↔ 2 H*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>3. C₆H₅F + H* ↔ C₆H₆* + HF*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>4. C₆H₅* + H* ↔ C₆H₆*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>5. C₆H₆* + * ↔ + C₆H₆</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>6. HF * ↔ HF</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td><strong>Model 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. C₆H₅F + * → C₆H₅F*</td>
<td>(RDS)</td>
<td></td>
</tr>
<tr>
<td>2. H₂ + 2 * → 2 H*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>3. C₆H₅F + H* → C₆H₆* + HF*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>4. C₆H₅* + H* → C₆H₆*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>5. C₆H₆* + * ↔ + C₆H₆</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>6. HF * ↔ HF</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td><strong>Model 3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. H₂ + 2 * → 2 H*</td>
<td>(RDS)</td>
<td></td>
</tr>
<tr>
<td>2. C₆H₅F + * ↔ C₆H₅F*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>3. C₆H₅F + H* → C₆H₆* + HF*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>4. C₆H₅* + H* → C₆H₆*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>5. C₆H₆* + * ↔ + C₆H₆</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>6. HF * ↔ HF</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td><strong>Model 4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. C₆H₅F + * ↔ C₆H₅F*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>2. H₂ + 2 * ↔ 2 H*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>3. C₆H₅F + H* → C₆H₆* + HF*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>4. C₆H₅* + H* → C₆H₆*</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>5. C₆H₆* + * ↔ + C₆H₆</td>
<td>(equilibrium)</td>
<td></td>
</tr>
<tr>
<td>6. HF * ↔ HF</td>
<td>(equilibrium)</td>
<td></td>
</tr>
</tbody>
</table>

2.3.6. Qualitative determination of modeled rate laws with respect to initial rate data

We attempted to evaluate each of the rate laws in Table 2.4 by using Excel's solver plugin to find best fit equilibrium constant and rate constant parameters.

Model 1A defines the rate determining step as C-F bond scission and asserts that the MASI is benzene. In Table 2.4, the derived rate equation for model 1A has a site blocking term of one plus the squared quantity of concentration of benzene over the equilibrium constant K₄. The
equilibrium constant, $K_4$, accounts for the thermodynamic process of surface benzene desorption into the liquid phase. In the initial rate regime where conversions are less than 10%, the concentration of benzene is negligible. Assuming the magnitude of $K_4$ is negligible the denominator goes to unity. Therefore, the rate law is first order in FB and half order in $H_2$. Model 1A is consistent with the dependence of the initial rate vs. FB concentration in the lower concentration regime, but whether it is the best fit at high concentration depends on the uncertainties in the initial rates.

Model 1B defines the C-F bond scission as rate controlling; however, the MASI is fluorobenzene. The final rate equation for model 1B, shown in Table 2.4, has a squared concentration of fluorobenzene term in the denominator multiplied by an equilibrium constant. Similarly, to model 1A, the initial rate at low concentrations is pseudo-first order in FB and may potentially describe the initial rate data shown in Figure 2.12A. As shown in Figure 2.12A, the initial rate becomes pseudo zero-order, and a F-test indicates that at a 95% confidence interval model 1B is a statistically better fit than model 1A. At higher concentrations the initial rate should become negative first order in FB, however, there is not enough data in the high FB concentration regime to test this supposition.

Model 2 also defines benzene as a MASI; however, the rate determining step is fluorobenzene adsorption to the surface. In Table 2.4, the final rate equation contains a site blocking term in the denominator defined as one plus concentration of benzene divided by the equilibrium constant $K_4$. There is an identical effect on the rate in the low conversion regime for model 2, as we predict in model 1A. Again, this is not consistent with the initial rate data in Figure 2.11, because the initial rate defined by the rate law should increase proportional to the initial FB concentration. Statistically it is equivalent to model 1A.

Model 3 was conceptualized to imagine a surface already saturated in FB, based on the initial state of our catalyst, which had been exposed for 10 min to a solution of FB and buffer without hydrogen. In this model the rate controlling step is assumed to be hydrogen dissociation
and the MASI is fluorobenzene. The predominant behavior should show first order dependence on hydrogen. We did not collect experimental data at variable hydrogen pressures; therefore, we cannot determine the order with respect to hydrogen pressure. The rate equation had a squared concentration of FB term in the denominator. To fit the data, the model applied a constant value of 2.6 atm for the hydrogen partial pressure. Based on initial fits using the constant hydrogen pressure value, this model is not consistent with the initial rate data of Figure 2.11, because it does not predict an increasing rate with initial FB concentration in the low FB concentration regime shown in Figure 2.12B. Indeed, the model predicts a slight decrease due to FB site blocking.

Model 4 is another example of a set of elementary reaction steps with the C-F bond breaking defined as rate controlling. A dual site blocking term contains hydrogen and fluorobenzene. Again, without variable hydrogen pressures, we are fitting a limited data set to this rate equation by holding the hydrogen pressure term constant. When the value of $K_2 P_{H_2}^{1/2}$ is small compared to the $K_1 P_{FB}$ term model 4 reduces to model 1B. As shown in Figure 2.12C, a fit as good as model 1B was obtained and the value of $K_2$ obtained $9E-6$ which seems physically plausible for a Henry’s law constant. As with model 1B, at sufficiently high concentrations, the squared dual site blocking term will cause the rate to decrease as the initial FB concentration increases and will have a partial order of -1.
initial rates of benzene production over multiple concentrations, using points in the initial linear regime are plotted as black open circles. A) initial values plotted with the models 1A, 1B, and 2. B) initial values plotted with model 3. C) initial concentrations plotted with model 4.

Models 1B and 4 show an acceptable overlay to the initial rate data shown in Figure 2.12A and D.

We next considered the adsorption limited rate law, equation 12, where FB is not in adsorption equilibrium. In the limit of the initial rate, the concentrations of benzene and HF approach zero, and the rate expression reduces to

\[ r = k^{FB}_{ads} \frac{P_{FB}}{1 + \sqrt{K_{H2}P_{H2}}} \]  

(18)

This expression is effectively first order in FB, since the hydrogen pressure was not varied, and the best fit curve, as shown in Figure 2.13, is a line with parameters \( k^{FB}_{ads} = 8 \times 10^{-6}, \sqrt{K_{H2}} = 0.1 \text{ atm}^{-1} \) with \( P_{H2} = 2.67 \text{ atm} \), and a Chi Squared of \( 1.01 \times 10^{-5} \). The line is identical to the fit in model 1A, which is not as good a fit as models 1B or 4.
2.3.7. Fitting acceptable models to raw data sets

Of the models considered, only models 1B and 4 were consistent with the initial rate data. We then extended our analysis to test whether these models can explain the [benzene] versus time data. The rate equation for model 1B was solved as a function of time starting from the initial concentration of each experiment and varying the kinetic parameters to predict the behavior. Since there are no hydrogen-varying data, we focused only on model 1B.

Figure 2.14 shows that model 1B can fit the lower FB concentrations in which the rate law is pseudo first order. In the higher concentration range the benzene production rate accelerates with time. For model 1B we fit two parameters, $K_1$ - defined as the equilibrium constant for FB adsorption- and $k_{app}$ - defined as $k_3K_1K_2^{1/2}P_{H_2}^{1/2}$. For both fitting parameters, model fit output values were to be greater than zero.

Figure 2.15 plots the highest FB concentration, 1.065 mM, versus time data. Under the constraint that $K_1 > 0$ the best fit line shows linear behavior. Model 1B cannot explain the
acceleration in the concentration of benzene ([benzene]) vs time data. The only way the best fit line will fit the raw data is at a non-physical negative value of $K_1$.

Although models 1B and 4 can explain the initial rate data, none of the models can fit the [benzene] vs time data. This poor model fit suggests that the chemical reactions occurring on the surface during the initial reaction period are more complex than can be analyzed via LHHW models, likely including reduction of the Rh nanoparticles, which are likely oxidized at the outset of the reaction.

![Figure 2.14](image)

Figure 2.14. Figure uses MATLAB ‘nlinfit’, to determine the fit line from the rate equations at an initial fluorobenzene concentration of 85 µM.
Figure 2.15. Figure uses MATLAB ‘nlinfit’, to determine the fit line from the rate equations at an initial fluorobenzene concentration of 1.06 mM.

2.3.8. Alternative explanations for auto-catalytic behavior

The observation of an increasing reaction rate at higher reaction concentrations is unusual but has been well documented in autocatalytic reactions. An autocatalytic reaction is defined as a chemical process in which a product of a reaction speeds up the reaction. For example, if the reaction increases the concentration of a reactant, then if the rate of the reaction depends on the concentration of the reactant this leads to an exponential growth in product generation. There are several possible ways that autocatalytic behavior could occur under the current reaction
conditions. From a modeling point of view, we consider three possible explanations and discuss the complexity required of each model.

The work from McNeill et al. gives several pieces of evidence that hydrogenation occurs only after C-F bond scission. These researchers ran isotope labeling studies and reactions with possible fluorocarbon surface intermediates. For example, they showed that fluorocyclohexane does not react under these conditions. One possibility for the C-F bond breaking process to be autocatalytic could require decomposition in the rate limiting step to have a vacant site adjacent to the surface intermediate. For example, if FB requires a vacant site for dissociation of the C-F bond to form a phenyl species and a fluorine adatom, then the rate controlling step is second order with respect to concentrations of FB and vacant sites. Further reaction of the phenyl species with adsorbed hydrogen would produce benzene and two empty sites after desorption. Adsorbed fluorine reacts with an adsorbed hydrogen producing HF, released into the bulk phase PBS, as well as two vacant sites. This reaction sequence would therefore produce four vacant sites. Overall, the concentration of vacant sites would triple and the rate of the rate controlling step would increase exponentially. Instances of autocatalytic reaction processes have been reported for decomposition of acetic acid on Rh (110), where the production of vacant sites causes the rate to exponentially increase.

Another possible explanation for an increasing rate is associated with the initial transient in the reaction. It is not clear whether the active state of the catalyst is Rh(0) or RhO$_2$. For example, it is possible that as the reaction proceeds and fluorine is removed from the substrate, a rhodium oxyfluoride is formed and that it is this form of the catalyst that is most active. This is a hypothesis that can be tested in further studies such as *in situ* XAFS at the Rh adsorption edge. In this framework, the catalyst state as received is likely to be the RhO$_2$ prior to introduction of hydrogen. Suppose that the oxide does not need to be reduced and the oxide is the active phase, similar to RuO$_2$ in CO oxidation. Under our experimental conditions, the catalyst surface was pre-equilibrated with FB, and at high initial concentrations, the FB coverage was relatively high as
indicated by the adsorption measurements shown in Figure 2.9. As hydrogen dissociates, fluorobenzene can react to form benzene which will desorb rapidly. Benzene desorption facilitates hydrogen dissociation, increasing the rate of reaction. At the threshold of roughly 450 µM, fluorobenzene adsorption could saturate active sites on the catalyst surface, leaving hydrogen unable to reach the surface and dissociate until after a benzene molecule desorbs. High FB coverage initially prevents the dissociative adsorption of hydrogen which is needed for the reaction mechanism. FB acts as a pseudo site blocking term but modeling the rate within the LHHW formalism does not take into account a high initial FB surface coverage to be the initial condition. In principle, the set of all coupled differential equations could be solved in a more complex microkinetic model.

A third possibility is based on the assumption that the active state of the catalyst is Rh metal. Considering that the state of the catalyst, as received, is RhO₂, reduction could not occur until the hydrogen was introduced. The reduction of RhO₂ to metallic Rh occurs at temperatures below 230 K. The catalyst was not pre-treated before being introduced into the reaction vial that already contained the fluorobenzene solution. After 10 min of stirring in the absence of hydrogen, FB will adsorb onto the surface (see Figure 2.9). If the active state of the catalyst is metallic Rh, there should be an induction time while RhO₂ is being reduced and the presence of FB at high substrate concentrations slows down the reduction rate. As the surface is reduced, however, the reaction rate speeds up. This hypothesis is consistent with our observations but requires testing by pre-reducing the catalyst before introducing the FB solution.

2.4. Conclusion

We successfully reproduced work by McNeill et al. that showed that Rh/Al₂O₃ was a highly efficient catalyst for catalyzing the room temperature defluorination of fluorobenzene. This hypothesis, put forth by McNeill, is counter-intuitive, but well supported by the data they provided. We successfully developed analytical methods that enabled us to measure the rate of benzene
production under a range of initial fluorobenzene concentrations. From a set of elementary reaction steps, we derived a set of LHHW rate equations, to describe multiple mechanisms. Models 1B and 4 showed an acceptable fit to the initial rate data and initial FB concentration data below 450 µM. However, neither showed an acceptable fit to the accelerating behavior of the rate at high initial concentrations of FB.

Further reactions should be done in the presence of a pre-reduced catalyst surface in the absence of fluorobenzene to test the hypothesis that a metallic Rh surface will produce a faster rate of HDF. In addition, we will reassess experimental details to improve reproducibility, such as fresh solution preparation of all stock solutions. In conclusion, this work positions the group to collect high quality data on the initial rates of defluorination and dechlorination of fluoro- and chlorobenzene to test the hypothesis put forth by McNeil et al. that the rate determining step of this reaction is not sensitive to C-X bond strength.

2.5. Future work

There are several aspects of this project that require further study before a mechanism can be proposed. Most importantly studies should be conducted to determine the active state of the catalyst. Studies should also be done to determine how fluoroarene species adsorb onto single crystal Rh. The studies can be done using techniques that include in situ XFAS at the Rh adsorption edge and single crystal XPS.

Further experiments in the batch reactor, with a pre-reduced catalyst surface would provide preliminary evidence to support whether RhO₂ or the Rh(0) catalyzes reaction. If batch experiments show evidence that the active state of the catalyst is Rh(0), future experiments with a pre-reduced catalyst in a packed bed flow reactor will afford more accurate and reproducible kinetics data, eliminating issues such as mass transfer, catalyst deactivation, and possible loss of gas-phase reactants (for a closed system attached to a GC-MS). Ultimately, collection of reproducible kinetics data would only be half of the evidence needed to propose a mechanism for
the hydrogenolysis of halo-arenes catalyzed by Rh/Al₂O₃. In addition to flow reactor kinetics data, density function theory (DFT) modeling of this reaction pathways on Rh single crystal and Rh/Al₂O₃ would provide further information that can be used to build a microkinetic model that describes surface adsorbate interactions via elementary reaction steps, activation energy barriers, and Gibbs’ free energy pathway diagrams. By thoroughly investigating the fundamental reaction kinetics both experimentally and computationally, future studies should be conducted to probe the effect of water in these hydrogenolysis reactions. Finally, through the development of a clear fundamental study of the hydrogenolysis of C-X aromatic bonds, future low-cost catalysts can be developed and implemented to begin to treat these low concentration pollutants in local/global water supplies. Future sustainable processes entail coupling the treatment of polluted water streams to engineered processes to make useful materials with a reusable low-cost catalyst.

2.6. Preliminary work

In a modified procedure, 1 mg of the same diluted catalyst was suspended in phosphate buffer solution (10 mM, pH=7.49) and exposed to 30 psi H₂ for 10 min while stirring at 1470 rpm. This pre-treatment step was added to reduce the RhO₂ to metallic Rh and cover the surface in dissociatively adsorbed hydrogen. After 10 min of stirring under H₂, 1 mL of a concentrated FB solution was added to the reaction vial to obtain similar initial substrate concentrations as in previous experiments. Addition of the substrate into the vial already under H₂, initiated the reaction. Initial reactant concentrations, the method for extraction into CH₂Cl₂, and sample analysis were kept the same.

Figure. 2.16 shows the trends for the rate of benzene production from a FB saturated catalyst surface and pre-reduced H₂ saturated surface. Preliminary data for the hydodechlorination of chlorobenzene (ClB) under the pre-reduced catalyst conditions show the initial rate of benzene production for fluorobenzene is much greater on the pre-reduced catalyst
(□) than under the conditions reported in this thesis (∆), strongly suggesting that Rh(0) is a more active phase of the catalyst. Furthermore, the initial rate of benzene production for ClB on the pre-reduced catalyst is substantially greater than for FB. This result suggests that the rate increases as the C-X bond strength decreases, as expected for saturated halocarbons. The lack of a significant difference in the rate of FB vs ClB dehalogenation in the work of McNeill et al, might be due to the initial rate being controlled by the rate of reduction of RhO₂ to Rh(0), since in their work as well as ours, the catalyst was not pre-reduced.

Figure 2.16. The initial rate of benzene production as a function of the initial concentration at conversions (<10%) for FB, with as received (∆) and reduced (□) diluted 5% Rh/Al₂O₃ : γ-Al₂O₃ (1:10), and ClB with pre-reduced dilute catalyst (○). Error bars represent the 95% confidence intervals from the weighted least squares fit of two or more replicates of [benzene] versus time data.
2.7. References


3.1. Course motivation—a personal reflection

On August 14, 2020, Barnard College announced that the Fall 2020 semester would be fully remote. Teaching remotely in the spring semester when NYC was the global epicenter of the COVID-19 pandemic was primarily a matter of surviving. Knowing that an entire semester of chemistry instruction would be fully on-line created a totally new set of challenges. The summer of 2020 was also marked by a high level of public awareness of the degree to which systemic racism remains pervasive in American public life, which also led to on-going public discussions of racism in science.\textsuperscript{40-43} In the late summer, seven students and recent alums sent the chemistry department a letter asking us to consider changes that would begin to dismantle racist practices within the department. (A copy of the letter is shared with permission of the authors, who have been anonymized, and included in Appendix C). As the chair of the chemistry department, one of us (RNA) knew we needed to offer a course that dealt with racism and chemistry. My next thought, after deciding we needed to offer a course on this topic, was that I was ill prepared to teach it. I was aware of some of the very thoughtful scholarship on antiracism and education and knew that I was not a scholar in that area. However, one of the things that impressed me as I read statement after statement from the Black Lives Matter (BLM) movement was how tired Black people were of explaining over and over the basic premises of racism in America. I kept reading that it was time for White people to do some of the work educating others about systemic racism. I agreed

\textsuperscript{a} This chapter was published in Babb, L. and Austin, R.N., 2022. Chemistry and Racism: A Special Topics Course for Students Taking General Chemistry at Barnard College in Fall 2020. \textit{J. Chem Ed.} 99 (1): 148-153
and decided to teach a course on racism in chemistry. Thus, in the face of the dual challenges of teaching chemistry online and the need to acknowledge that black lives matter, the Department of Chemistry at Barnard College offered BC CHEM 1004 Special Topics: Chemistry and Racism for the first time in Fall 2020. The course was not a direct response to the request from students and alums but was rather the first step in accepting their invitation to engage.

Figure 3.1 Graphical abstract. Reproduced [with permission] from Babb et al.

3.1.1. Objectives of the course

The objectives of the course were to provide students with an opportunity to discuss racism and chemistry and to offer recommendations to the department for ways to change practices and pedagogy to make the department less racist and to create environments that would be more inclusive and enable more students to flourish. The course provided opportunities for students to discuss topics of accessibility and inclusivity more broadly with professors and administrators and to collaboratively strive for equity in the classroom.
3.1.2. How the course was constituted

This course was one of five different special topics courses that were created and offered concurrently with general chemistry (BC CHEM 2001) in order to create small seminar-style experiences that linked general chemistry with topics that lent themselves to more active student engagement. Table 3.1 provides a list of the special topics courses and information on student enrollment. All of the special topics courses were taught by the instructor of general chemistry. She had no special expertise in anti-racist pedagogy and had not taught a course like this before. She was, however, a member of a task force charged with advising the provost on academic matters during the pandemic and in that role had reviewed a college-wide survey of student experiences in the spring. Student comments about what worked, and more importantly, what had not worked during the spring, were particularly helpful in shaping this course and the fully remote general chemistry course to which it was connected.

Table 3.1. Summary of Special Topics Courses Offered in Fall 2020 to Accompany General Chemistry

<table>
<thead>
<tr>
<th>Course Name</th>
<th>Number of Students Enrolled</th>
<th>Auditing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry and Racism</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>The Chemistry of Color</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>The Chemistry of Covid-19</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>An Introduction to Chemical Engineering</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>The Chemistry of Lead</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

The special topics courses were listed in the course catalog and advertised in an event the college termed “Launch Week”, where individual departments presented information to students about what a fully remote fall would look like and the ways in which instruction had been changed in light of the lessons learned from the crisis mode in which online learning occurred in the second half of the spring semester. The college also compiled and distributed to students a
list of courses covering content on COVID-19 and BLM for interested students, and this course was included in that list.

3.2. What happened in the course

The course was a six-week, 0.5 credit, P/F course that met once a week for an hour. It was co-facilitated by a recent alum who is currently a Ph.D. candidate in chemistry. There were 12 students taking the class for credit. Of these, all but one was currently enrolled in general chemistry and all but one was in their first or second year in college (see Table 3.1 for summary of participation data). Several other interested chemistry majors joined the class occasionally. Guest speakers were brought in to enrich and give perspective on discussion topics relating to institutional change.

The dream was to dismantle racism in chemistry (see Figure 3.1). The goal was to participate in dismantling racism in chemistry at Barnard College. To do that, four basic pillars undergirded our project. We wanted students to be aware of the issues and to have a knowledge of relevant history. Weeks 2 and 3 provided students with the opportunity to learn about the issues. Week 4 provided students with an opportunity to become knowledgeable of relevant history. We thought it important to acknowledge systemic racism, which was something we did in every class. We also thought it important to provide opportunities to discuss and listen. Again, this was something we did in every class. Table 3.2 provides a week-by-week overview of what was covered. Table 3.3 provides an overview to the topics that emerged in each class in response to these themes.
Table 3.2. Overview of Week-by-Week Activities

<table>
<thead>
<tr>
<th>Week</th>
<th>Module Theme</th>
<th>Assigned Readings/Multi-Media Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A sense of the landscape</td>
<td>Town Hall Zuckerman Institute&lt;sup&gt;a&lt;/sup&gt; &lt;br&gt; Petition to Barnard STEM Department &lt;br&gt; Petition to Barnard Chemistry Department &lt;br&gt; Picture a Scientist documentary&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Representation in chemistry departments in the United States</td>
<td>Demographics data from Oxide&lt;sup&gt;c&lt;/sup&gt; &lt;br&gt; ACS Resources&lt;sup&gt;d&lt;/sup&gt; &lt;br&gt; Two editorials on diversity in chemical publishing&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>Voices and histories of Black American chemists</td>
<td>Black American Chemists&lt;sup&gt;f&lt;/sup&gt; &lt;br&gt; 9 Black Chemists You Should Know About&lt;sup&gt;g&lt;/sup&gt; &lt;br&gt; Beyond Small Numbers: Voices of African American Ph.D. Chemists&lt;sup&gt;h&lt;/sup&gt; &lt;br&gt; Turning isolation into inclusion&lt;sup&gt;i&lt;/sup&gt; &lt;br&gt; #BlackinChem&lt;sup&gt;j&lt;/sup&gt; &lt;br&gt; Nurturing black chemists (&lt;i&gt;CEN&lt;/i&gt;)&lt;sup&gt;k&lt;/sup&gt; &lt;br&gt; Stemnoire&lt;sup&gt;l&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>Reconstructing organizations to create change</td>
<td>&lt;i&gt;Harvard Business Review&lt;/i&gt; article on change in institutions&lt;sup&gt;m&lt;/sup&gt; &lt;br&gt; Study on faculty beliefs about intelligence and effects on racial achievement gaps in STEM classes&lt;sup&gt;n&lt;/sup&gt; &lt;br&gt; ACS actions&lt;sup)o&lt;/sup&gt; &lt;br&gt; Ten simple rules for building an antiracist lab&lt;sup&gt;p&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Recommendations to Barnard College</td>
<td>No readings assigned</td>
</tr>
<tr>
<td>6</td>
<td>Final reflections, final recommendations</td>
<td>No readings assigned</td>
</tr>
</tbody>
</table>

<sup>a</sup>See ref 49. <sup>b</sup>See ref 50. <sup>c</sup>See ref 51. <sup>d</sup>See ref 52. <sup>e</sup>See refs 48 and 53. <sup>f</sup>See ref 62. <sup>g</sup>See ref 57. <sup>h</sup>See ref 56. <sup>i</sup>See ref 61. <sup>j</sup>See ref 66. <sup>k</sup>See ref 58. <sup>l</sup>See ref 67. <sup>m</sup>See ref 63. <sup>n</sup>See ref 65. <sup>o</sup>See ref 68. <sup>p</sup>See ref 64.
Table 3.3. Overview of Course Themes and Ideas That Emerged from the Discussion of Those Themes

<table>
<thead>
<tr>
<th>Topic</th>
<th>Keywords from Discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Representation in chemistry departments in the United States</td>
<td>Liberal arts versus engineering, BIPOC faculty cluster hire, Tenure process, Grant funding</td>
</tr>
<tr>
<td>Voices and histories of Black American chemists</td>
<td>Tokenism, Academic, Intersectionality, Responsibility</td>
</tr>
<tr>
<td>Reconstructing organizations to create change</td>
<td>Longevity of equitable practices, Addressing bias, Removing the burden from the BIPOC community</td>
</tr>
<tr>
<td>Recommendations to Barnard College</td>
<td>Reforming introductory STEM education, Valuing and encouraging student input</td>
</tr>
<tr>
<td>Course reflections and reading the final letter</td>
<td>Gratitude, Inspiration, Accountability</td>
</tr>
</tbody>
</table>

The class began by considering the current state of affairs in science in the United States and in the department. Students watched a recording of a recent town hall meeting\(^{49}\) (June 11, 2020) at the Zuckerman Institute at Columbia (Barnard College and Columbia University are affiliated with each other) where Professors Robert E Fulilove (Professor of Sociomedical Sciences at Columbia University Medical Center and Associate Dean Community and Minority Affairs) and Professor Olajide Williams (Professor of Neurology and co-Director of Columbia’s Community Wellness Center) discussed the interactions between racism, history, public health equity, and justice.\(^{44}\) While their conversation was not strictly about chemistry, it did focus on science and public health and the local setting helped reinforce the idea that the class was going to focus on both the global and the local. Students in the class also read the letter that had been sent to the department from students and alumni. They used the first class meeting to set ground rules for
discussion. Students were also given the opportunity to attend a virtual private screening of the 2020 film, *Picture a Scientist*.⁵⁰

Class discussions every week after the first week were led by a team of two to three students, selected at random at the beginning of the semester. (Table C.1 in the Appendix C provides a list of the discussion questions generated by the students, which could be adapted and modified if the course were taught at another institution). The second class focused on the issue of representation in chemistry departments in the United States. Data compiled by Oxide (the Open Chemistry Collaborative in Diversity Equity⁵¹) formed the bulk of the material students reviewed before class. Secondary readings included a recent letter from the 2020 ACS President Luis Echegoyen on ACS commitments and actions to diversity, inclusion, and respect⁵² and a recent essay in the *Journal of the American Chemical Society* written by Professor Melanie Sanford⁵³ about an “actions not words” approach to equity and inclusion in the chemical sciences. Students learned about career stages, academic ranks, tenure, and the process of receiving grants and the career implications associated with grant funding. This information provided important context to the demographic information provided, where students observed the obvious discrepancies.⁵⁴,⁵⁵

In the third week, students considered the voices and histories of Black American chemists. Students read a selection from the book *Beyond Small Numbers, Volume 4: Voices of African American Ph.D. Chemists* by Willie Pearson, Jr.⁵⁶ They also read an article from *Chemistry and Engineering News (CEN)* “Nine Black Chemists You Should Know”⁵⁷ and a small series in *CEN* titled “Nurturing Black Chemists”⁵⁸–⁶¹ and a photoblog that highlights Black American chemists throughout history.⁶²

Students opened the discussion with a series of complex questions, such as:

- “How do we distinguish between progress and trying to fill quotas?”
• “How do we move the responsibility of including Black people in STEM away from Black people themselves to non-Black individuals?”

• “How do we take the responsibility off Black students in STEM to be the face of all Black students in STEM?”

• “How do we promote Black women in academia?”

Four major themes of tokenism, academia, intersectionality, and responsibility emerged in the student-led discussion.

The fourth week students read a selection of articles about best practices in creating institutional change. The Director of the Center for Engaged Pedagogy at Barnard College (Dr. Jennifer Rosales) attended class and offered her perspective on best practices for effective pedagogical change. These readings prompted our students to reflect on how the life experiences of a professor impacts their quality of learning and even perhaps the scientific information we learn.

After getting a sense of the broader context, the last two weeks of the semester were refocused on the Barnard-specific context. Students revisited the recommendations made in the letter to the department from the summer and reaffirmed their sense for the importance of some of the recommendations, recognized that some recommendations were not needed because resources already existed or actions had already been taken, and were conflicted about others.

Assignments consisted of a weekly ungraded free write reflection in response to the prompt: “Take a moment to write about your thoughts from what you read, heard, or discussed this week. Reflect on what brought you to this course and how your thoughts are changing” and the upcoming student facilitator team had to submit discussion questions to the co-facilitators.
3.3 The impact of the course on the people who participated in it and the specific recommendation that arose from the course

3.3.1. Students

Student reflections throughout the course and at the end were extraordinarily thoughtful and indicated that students were engaging seriously with the course material. A selection of student reflections is included below (with permission of the students, whose names have been removed). These are just a few of the very thoughtful comments students offered in their weekly reflections. Reading how deeply students were thinking about the class material was one of the most rewarding aspects of facilitating this course.

When we looked at the Oxide data from this week, I was taken aback by how stark the gap between women/people of color and white men was. Although I've always been aware that academia is white male-dominated, viewing the problem through a quantitative lens emphasized that disparity. I was especially startled by the gap in faculty between black faculty and other races. The African-American column on the Oxide data sheet for underrepresented minorities quite literally looked like binary code, because the number of black faculty members at the recorded universities were almost exclusively 0 and 1. This data is clear supporting evidence that, despite what many university diversity brochures may advertise, academia remains the white man's territory, where women and underrepresented races are tolerated, but not necessarily welcomed. To address the lack of diversity, universities should review their hiring practices and actively recruit underrepresented individuals for faculty positions.
I joined this course to supplement general chemistry and to become better educated about the obstacles people of color face in chemistry. As a white woman who grew up in a predominantly white area, I want to learn more about how race impacts life, especially in career fields I’m interested in. So far, the course has been very insightful and thought-provoking. I found this week particularly valuable because I was exposed to a lot of people that, sadly, I’d never really heard about before…. Hearing the stories and perspectives of both living and historical Black chemists has been a great experience and I hope to continue to learn more names and stories in the second half of our 6-week course.

I liked the article that discussed the importance of employing growth mindset practices more in the classroom. In our past few meetings, a lot of people discussed their frustration at the fact that the sciences are known notoriously for being used to unfairly “weed out” those who are deemed less capable. Working to implement growth mindset practices everywhere could help dismantle this exclusive stereotype that looms over the field of science and deters prospective scientists from entering.

I think in general, this growth mindset should be implemented everywhere and not just in the classroom. There must be greater support systems for BIPOC even when they graduate and leave the school environment. This way we can ensure the long-term maintenance of diversity in the sciences.
This week I really enjoyed being able to create the discussion questions with my peers, because it allowed me to critically think about everything I had read for class and come up with ways to discuss the important topics with everybody. I thought our discussion about how STEM classes are often set up to “weed people out” and how this creates even more exclusion in the field was interesting. Something that I noticed in class was that none of the questions we asked had easy answers, but just having people begin to think about those topics and discuss them with other people is a great way to start moving in the right direction. The problems we are trying to address in this class, won’t be easy fixes, but the fact that people have signed up for this class in the first place is a great first step. This class has made me realize how many other subjects intersect with the STEM field and has made me want to further pursue classes that can be applied to Biology or Chemistry in an interdisciplinary way so I can continue to think critically about the field I hope to enter. I think that if everyone that held any power in STEM academia and anyone that ever wants to end up having a career in STEM were to take a class like this, or have questions like this posed to them, things would begin to change. The more minds working towards a common goal, the better.

The course was evaluated using the standard Barnard and Columbia College course evaluation form. Students are asked to rate the course and the instruction in a variety of ways on a scale of 1 (poor) to 5 (excellent). Information about the college averages for all questions are also provided to the instructor along with anonymized versions of the responses after grades are submitted. We also reflected on the class in our last session together. Overall, students were very positive about the course with the mean student response being above the college mean for all questions except for question 17 (“How much has the course increased your interest in the broader intellectual field?”) where the response was very similar to the college average, and
questions 18–20 (“How much has the course increased your quantitative, presentation, and writing skills?”), which were unrelated to the course aims. (A summary of the survey instrument and student responses is provided in the Supporting Information).

The students who wrote about why they took the course mostly mentioned being interested in the subject and not knowing much about it, so wanting to learn more. When asked what they valued most about the course, most students mentioned that they really valued being part of a process of creating actual change in the department. Students appreciated the intense and open discussions and very much felt that as a result of the course they could collaborate with peers to develop solutions to problems.

Many students mentioned that the course inspired them to put in extra time and effort because the topic was so relevant and in the words of one student “infuriating” that they wanted to read as much as they could to be as impactful as possible. Students appreciated that they were sent additional readings when they expressed interest in a topic. One of the students in the course has been working with faculty in the department in which she is majoring in (neuroscience) to try to replicate the course in some form in that department. Students valued the centrality their voices played in the way the class was taught.

3.3.2. Co-facilitator perspective

As a co-facilitator of this course, and recent graduate of the college, one of us (LB) interacted with prospective majors and provided them with social insights into the field of chemistry as I had experienced it as a graduate student. Intersectionality was a concept that our students eagerly embraced on the first day of classes. As this was an intimate seminar style course led by student facilitators, we challenged our students to bring their discomfort, confusion, and frustrations into the space. Each week we engaged with students’ personal reflections and remarks on assigned readings that empowered us all to face uncomfortable truths and postulate anti-racist solutions we can implement as students, educators, and administrators. One student who is thinking
contrary to social norms may be ignorable, but an entire generation of students might just change the status quo. Envision those students eventually growing to be educators and possibly administrators, challenging their peers along the way to be equitable in their classrooms, labs, and staff meetings. How do we begin to progress in a system that has such small margins for opportunity and peer-acknowledged excellence? One way is to make spaces that welcome students, alums, faculty, staff, and interested community members to talk about it, write about it, and recommend ways to promote equitable practices in our institution.

3.4. Discussion of major takeaways

These three major takeaway ideas emerged from the class:

- We need to talk about racism and inclusion (a lot)
- Institutions need to truly prioritize inclusion and diversity—weave it into the core mission and budget
- Structural racism exists, but can be dismantled

The opening lines of the Zuckerman town hall[^49] that students watched reinforced the idea that academic institutions go through the same patterns of incident to concerns to committee formation to committee report to moderate to no action over and over. This course strove to have an impact and focusing on our local context was grounding. Our general impression of the course was that it served several important needs. It provided a small seminar-like space where students could discuss racism and chemistry. It also helped the department think about the issues raised in the student/alumni letter, which in turn has led to changes.

3.4.1. The impact of the course on the department and its efforts to dismantle racism

The clearest takeaway from the course is that there need to be regular opportunities for students in chemistry to talk about racism. While it is obvious to every chemistry teacher that each
year a new group of students needs to learn about atomic and molecular orbitals, sometimes there is an unexamined sense that if racism and chemistry has been discussed once, that should be enough. It is not. This was the single most unequivocal lesson we learned from our students. We are committed to holding meetings every semester with our students to discuss diversity and inclusion in our department.

This course influenced General Chemistry (BC CHEM 2001). It motivated the creation of problem sets that were connected to the research of current diverse chemists who were featured in the weekly problem sets. It also reinforced the wisdom of eschewing timed closed book exams during the pandemic when intrusive online monitoring would have been required and opened up the broader question of the value of closed book timed exams in general chemistry.

The course has influenced who the department invites for seminar speakers. We are making it a priority to invite more BIPOC seminar speakers and also to invite seminar speakers who are not academics in an effort to make clear that training in chemistry provides a strong foundation for work in many different fields. The department has been working on inclusionary ways to present candidates for tenure that reflect our commitment to fostering a truly equitable research/learning community, and the course reinforced the importance of this. The course has led the department to prepare a roadmap to help students better navigate the system and has been talking with administrators about creating a college-wide model for disseminating this information. We have also been fortunate in that the college has recently created a single shop office called “Access Barnard”. We have been working with that office to provide free model kits and calculators and copies of software to students with unmet financial needs.

We hope this course will inspire the creation of an interdisciplinary course co-taught by faculty from STEM, Ethnic Studies, and/or Women, Gender, and Sexuality Studies departments to examine the social, historical, and political context of racism in science. If we are to improve diversity and representation within the field, perhaps addressing topics of access and historical exclusivity early in students’ degree-seeking programs might positively impact the demographic
representation of future generations of scientists. Conversations among interested faculty in different departments are underway.

3.5. Parting thoughts

When we began working on the course, we did not find many other models in chemistry. The only relevant course we found is a course entitled Being Human in STEM,69–71 which began at Amherst College but has now spread to a few other institutions. A search of this Journal found no examples of courses on racism in chemistry. We hope that publication of this article will inspire more non-BIPOC chemists to take the necessary step of moving from statement to action, drawing on the resources and roadmap we have provided as helpful tools for others beginning this work. We have been inspired by our experiences teaching this course and welcome the opportunity to participate with others in the chemistry community to dismantle racism in chemistry.

3.6. References

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4.1. Critical commentary: honoring the immeasurable: bell hooks’ feminist pedagogy in teaching

_Unexpected co-conspirators, speaking together_: Fall 2021. Nondescript classroom, nondescript campus. The first day of a very descript “Black Feminist Thought and Expression” (BFTE) course (Figure 4.1). In class, we gather stories about our names, reaching for roots... We share the story of BFTE, (its/our) becoming on this white-serving campus, occupying indigenous lands. We are three educators/learners you may not expect would come together as BFTE’s co-teachers – a Black chemistry graduate student, a white mathematics part-time faculty, and a white non-U.S. communication studies assistant professor.

We learn, with hooks and Scapp, that unlikely friendships and dialogues of difference can be made generative, that embodiment and emotion are knowledge, that who and what we carry with ourselves in educational spaces is consequential and always changing “in a dialogue with a world beyond itself”.68 We enter the classroom, bringing our differences and a shared commitment to hooks’ pedagogical vision.

_bh_: ... _education can only be liberatory when everyone claims knowledge as a field in which we all labor._73

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72 After Boylorn (2016), we use the OneWord spelling to highlight the both/and of race/gender.

a This chapter was accepted for publication in Babb, L.; Herakova, L.; Roberge, K. Academic Spaces of Possibility? 2022. A Proleptic Dialogue with BlackFeminism at the Center. Feminist Pedagogy
We start BFTE by reading *Engaged Pedagogy*, together, aloud. hooks’ voice fills the classroom, echoes through the semester. It is in-tense: How do we center BlackFeminism and students, while decentering whiteness in this mostly white-bodied, whiteness-trained classroom? It is dialogically in-tense: demanding our attention to the arrays of voices in us, the texts we select, the practices we engage, the learners we invite and become. It is a proleptic dialogic tension: “simultaneously existing in the present, past, and future (...) individual and collective acts of remembering and embodying”. We hear proleptic dialogues when hooks speaks with collaborators and with her own whole embodied selves – as a BlackWoman, student, teacher, scholar – within and across texts (Figure 4.2). She is teaching us an ethic of “returning to the body” – dialogically, in-relation, in-tension, engaging “ourselves as subjects in history”.73
Moving toward this ethic, in BFTE, we seek proleptic dialogic knowing not only or even primarily interpersonally, but through embodied intentional silences, creative and reflexive expressions, autoethnographies, quotes quilting, mapping (Figures 4.3 and 4.4). We are growing BFTE into connected homeplaces for BlackFeminist pedagogy.

*LB*: For me, BFTE begins as an intentional response to my pain of alienation – here, there are few physical spaces centering care and community-building around Black herstory. I have deep relationships with BlackFeminists like Lorde, Collins, Sanchez, Gumbs, and want to center the joy and healing of their words and beings. In my vision, I crave/carve a BlackWoman place.

But then... I was the only BlackWoman in the classroom, longing to *belong*. My knowing/feeling body was precariously out-of-place, again. I had imagined the power of my relationship to BlackFeminism radiating, growing as a living/life force rooting in learners’

---

*BFTE learners created quotation quilts (fig. 2 and 4) and learning maps (fig. 3) to trace dis/connections among texts and/or experiences. Both activities begin with identifying a theme. Then, individually and/or together, we craft visual placements of/for conversing ideas. Quotation quilts imagine proleptic dialogues – we begin with quotes from a central text and then “stitch” quotes from other texts that amplify what is said, challenge it, or move us to consider it differently.*
embodied experiences. But in that overwhelmingly white classroom, in the belly of a pandemic with dangerous physicality, we were hyper-conscious of race, conscious of masked, closed bodies. The distance depleted me.

*bh*: For those who dominate and oppress us benefit most when we have nothing to give our own, when they have so taken from us our dignity, our humanness that we have nothing left, no 'homeplace' where we can recover ourselves.75

*LH*: Lauren, when you said the physical classroom was not a (home)place for your blackgirl72 body, the class was taut. We knew it with our postures: rigid, silent in the small desks, at 9.30 am, with winter chomping daylight. We had to become “designers” – “actors who intentionally organize space and make deliberate decisions about the teaching/learning experiences [of] others”.74 This wasn’t about finding different bridges, it was, to borrow embodiment from the seminal *This Bridge Called My Back*77, that we – each a knower/learner – needed to stretch and strengthen our backs over different connecting streams, to become connectors differently.

*KR*: Early in the course, we introduced Gottman’s feelings wheel and the window of tolerance to help us name sensations as we experience texts and each other. Initially, I felt stuck in the “scared” sector of that wheel, but by the time Lauren facilitated the kitchen-table-talkc, I found myself also in “joy.” I had been moving towards home/work72 as the “classroom” came to mean learning places that included the home of my own body of whiteness. Home/work was private in-and out-of-class autoethnographic inquiry that facilitated embodied learning while precluding centering whiteness in our shared classroom space. Home/work was writing, creating, acknowledging the dis/connecting potential of my white body as a site of/for knowledge. Perhaps students moved to/with home/work similarly as they sought and shared connections to BlackFeminism where it mattered to them – country music, running, drag...

---

c “Black Feminism and me/ME,” available at https://www.youtube.com/watch?v=g-sju1kuy0k
LB: However, while we successfully centered BlackFeminist voices and knowledge in the physical classroom, this space was still not a homeplace for my blackgirl body. I turned my back sideways to this classroom and began bridge-building dialogic podcasts with other BlackFeminists discussing BFTE texts. Through this and our alternative Friday Zoom classes, we stretched and twisted the classroom into connected spaces, crafting something of a “homeplace” for me.

bh: When black women renew our political commitment to homeplace, we can address the needs and concerns of young black women who are groping for structures of meaning that will further their growth, young women who are struggling for self-definition.\textsuperscript{75}

LB: Without exposing myself in the physical classroom, the podcasts were blackgirl gathering spaces. Prioritizing intellectual rigor and care, they grew into teaching tools, guiding by example about meaningfully relating personal experiences to BlackFeminist texts.\textsuperscript{73} At semester’s end, I facilitated a public intergenerational kitchen-table-talk among BlackFeminists celebrating our commitment to sharing the joys and knowledge our bodies collect over time and for future times. Our distinct “ways of knowing” had common threads that wove ... a sistah-hood of poetic blackgirl magic (Figure 4.4).
Together: We started, like most college classes, with/in a nondescript institutionally-assigned room... We co-created multiple connected places where body-rooted dialogues are continuing as in-tense possibilities.

bh: We can make homeplace that space where we return for renewal and self-recovery, where we can heal our wounds and become whole.\textsuperscript{75}

Figure 4.4 Quotation quilt: BFTE Homeplace
4.2. References


REFERENCES


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APPENDICES

Appendix A

C-F HYDRODEFLUORINATION

A.1. Rate derivations

A.1.1 [Model 1A] C-F bond breaking is the rate limiting step with benzene as MASI

Elementary Reaction Steps:

1. $\text{C}_6\text{H}_5\text{F} + * \leftrightarrow \text{C}_6\text{H}_5F*$ (equilibrium)
2. $\text{H}_2 + 2 * \leftrightarrow 2 \text{H}*$ (equilibrium)
3. $\text{C}_6\text{H}_5\text{F} * + \text{H} \rightarrow \text{C}_6\text{H}_6 *$ (RDS)
4. $\text{C}_6\text{H}_5 * + \text{H} \leftrightarrow \text{C}_6\text{H}_6 *$ (equilibrium)
5. $\text{C}_6\text{H}_6 * \leftrightarrow * + \text{C}_6\text{H}_6$ (equilibrium)

The rate is defined by the irreversible step, step 3.

$\text{rate} = k_3\theta_{\text{FB}}\theta_{\text{H}}$ (19)

The most abundant surface intermediate (MASI) is defined as benzene.

$1 = \theta_* + \theta_{\text{B}}$ (20)

Equilibrium constants are defined as the ratio of the products over the reactants, where theta represents a molecule on the surface-active site. And theta (*) represents an empty surface-active site.

$K_1 = \frac{\theta_{\text{FB}}}{p_{\text{FB}}\theta_*}$ (21)

$K_2 = \frac{\theta_{\text{H}}^2}{p_{\text{H}_2}\theta_*^2}$ (22)

$K_4 = \frac{p_{\text{B}}\theta_*}{\theta_{\text{B}}}$ (23)

To re-express the rate in terms of equilibrium constants and partial pressures, plug in equilibrium constants, equations (21-22) into rate equation (19):

$r = k_3K_4^{1/2}p_{\text{FB}}^{1/2}b_{\text{H}_2}^{1/2}\theta_*^2$ (24)
Rearrange equation (20) to solve for the theta (*) quantity, and substitute in the re-arranged equilibrium constant equation (23) that defines the MASI species.

\[
\theta_* = \frac{1}{1 + \frac{P_B}{K_4}}
\]  

(25)

Substitute equation (25) into the rate equation (24) to define the final rate equation (26) in terms of equilibrium constants, partial pressures, and a rate constant.

\[
r = \frac{k_3 K_1 K_2^{1/2} P_{FB}^{1/2} P_{H_2}^{1/2}}{(1 + \frac{P_B}{K_4})^2}
\]  

(26)
A.1.2. [Model 1B] C-F bond breaking is the rate limiting step with fluorobenzene as MASI

Elementary Reaction Steps:

1. $C_6H_5F + * \leftrightarrow C_6H_5F^*$ (equilibrium)
2. $H_2 + 2* \leftrightarrow 2H^*$ (equilibrium)
3. $C_6H_5F^* + H \rightarrow C_6H_6^*$ (RDS)
4. $C_6H_5^* + H \leftrightarrow C_6H_6^*$ (equilibrium)
5. $C_6H_6^* \leftrightarrow \emptyset + C_6H_6$ (equilibrium)

The rate is defined by the irreversible step, step 3.

rate = $k_3\theta_{FB}\theta_H$  \hspace{1cm} (27)

The most abundant surface intermediate (MASI) is defined as fluorobenzene

$1 = \theta_* + \theta_{FB}$  \hspace{1cm} (28)

Equilibrium constants are defined as the ratio of the products over the reactants, where theta represents a molecule on the surface-active site. And theta (*) represents an empty surface-active site.

$K_1 = \frac{\theta_{FB}}{p_{FB}\theta_*}$  \hspace{1cm} (29)

$K_2 = \frac{\theta_H^2}{p_{H_2}\theta_*^2}$  \hspace{1cm} (30)

$K_4 = \frac{p_B\theta_*}{\theta_B}$  \hspace{1cm} (31)

To re-express the rate in terms of equilibrium constants and partial pressures, equations (29-30) into rate equation (27):

$r = k_3K_1^{1/2}p_{FB}^{1/2}\theta_*^{1/2}$  \hspace{1cm} (32)

Rearrange equation (28) to solve for the theta (*) quantity, and substitute in the re-arranged equilibrium constant equation (31) that defines the MASI species.

$\theta_* = \frac{1}{(1 + \frac{p_{FB}}{K_2})}$  \hspace{1cm} (33)
Substitute equation (33) into the rate equation (32) to define the final rate equation (34) in terms of equilibrium constants, partial pressures, and a rate constant.

\[ r = \frac{k_3 K_1 K_2^{1/2} P_B P_{H_2}^{1/2}}{(1 + \frac{P_B}{K_4})^2} \]  

(34)
A.1.2. [Model 2] Fluorobenzene adsorption is the rate limiting step with benzene as a MASI

Elementary Reaction Steps:

1. \( \text{C}_6\text{H}_5\text{F} + \ast \leftrightarrow \text{C}_6\text{H}_5\ast \) (RDS)
2. \( \text{H}_2 + 2 \ast \rightarrow 2 \text{H} \ast \) (equilibrium)
3. \( \text{C}_6\text{H}_5\text{F} \ast + \text{H} \ast \rightarrow \text{C}_6\text{H}_6 \ast \) (equilibrium)
4. \( \text{C}_6\text{H}_5 \ast + \text{H} \ast \leftrightarrow \text{C}_6\text{H}_6 \ast \) (equilibrium)
5. \( \text{C}_6\text{H}_6 \ast \leftrightarrow \ast + \text{C}_6\text{H}_6 \) (equilibrium)

The rate is defined by the irreversible step, step 1.

\[
\text{rate} = k_1P_{\text{FB}}\theta_* \tag{35}
\]

The most abundant surface intermediate (MASI) is defined as benzene

\[
1 = \theta_* + \theta_B \tag{36}
\]

Equilibrium constants are defined as the ratio of the products over the reactants, where theta \( \ast \) represents a molecule on the surface-active site. And theta \( \ast \) represents an empty surface-active site.

\[
K_2 = \frac{\theta_H^2}{P_{\text{H}_2}\theta_*^2} \tag{37}
\]

\[
K_4 = \frac{P_{\text{B}}\theta_*}{\theta_B} \tag{38}
\]

Rearrange equation (36) to solve for the theta \( \ast \) quantity, and substitute in the re-arranged equilibrium constant equation (38) that defines the MASI species.

\[
\theta_* = \frac{1}{P_{\text{B}} \left(1 + \frac{\theta_B}{K_4}\right)} \tag{39}
\]

Substitute equation (39) into the rate equation (35) to define the final rate equation (40) in terms of equilibrium constants, partial pressures, and a rate constant.

\[
r = \frac{k_1P_{\text{FB}}}{\left(1 + \frac{P_{\text{B}}}{K_4}\right)} \tag{40}
\]
A.1.3. [Model 3] Hydrogen surface dissociation is the rate limiting step with fluorobenzene as the MASI

Elementary Reaction Steps:

1. \( \text{H}_2 + 2\ast \leftrightarrow 2\text{H} \ast \) (RDS)
2. \( \text{C}_6\text{H}_5\text{F} + \ast \rightarrow \text{C}_6\text{H}_5\text{F} \ast \) (equilibrium)
3. \( \text{C}_6\text{H}_5\text{F} \ast + \text{H} \ast \rightarrow \text{C}_6\text{H}_6 \ast \) (equilibrium)
4. \( \text{C}_6\text{H}_5 \ast + \text{H} \ast \leftrightarrow \text{C}_6\text{H}_6 \ast \) (equilibrium)
5. \( \text{C}_6\text{H}_6 \ast \leftrightarrow \ast + \text{C}_6\text{H}_6 \) (equilibrium)

The rate is defined by the irreversible step, step .

rate = \( k_1\text{P}_{\text{H}_2}\theta_\ast^2 \) (41)

MASI

\( 1 = \theta_\ast + \theta_{\text{FB}} \) (42)

Equilibrium constants are defined as the ratio of the products over the reactants, where theta represents a molecule on the surface-active site. And theta (*) represents an empty surface-active site.

\( K_1 = \frac{\theta_{\text{FB}}}{P_{\text{FB}}\theta_\ast} \) (43)

Rearrange equation (42) to solve for the theta (*) quantity, and substitute in the re-arranged equilibrium constant equation (42) that defines the MASI species.

\( \theta_\ast = \frac{1}{(1+K_1P_{\text{FB}})} \) (44)

Substitute equation (44) into the rate equation (41) to define final rate equation (45) in terms of equilibrium constants, partial pressures, and a rate constant.

\( r = \frac{k_1\text{P}_{\text{H}_2}}{(1+K_1P_{\text{FB}})^2} \) (45)

Elementary Reaction Steps:

1. \( \text{C}_6\text{H}_5\text{F} + * \leftrightarrow \text{C}_6\text{H}_5\text{F}^* \) (equilibrium)
2. \( \text{H}_2 + 2* \leftrightarrow 2\text{H}^* \) (equilibrium)
3. \( \text{C}_6\text{H}_5\text{F}^* + \text{H}^* \rightarrow \text{C}_6\text{H}_6^* \) (RDS)
4. \( \text{C}_6\text{H}_5^* + \text{H}^* \leftrightarrow \text{C}_6\text{H}_6^* \) (equilibrium)
5. \( \text{C}_6\text{H}_6^* \leftrightarrow * + \text{C}_6\text{H}_6 \) (equilibrium)

The rate is defined by the irreversible step, step 3:

\[
\text{rate} = k_3 \theta_{\text{FB}} \theta_{\text{H}^*} \quad (46)
\]

Defining Surface Species

\[
\theta_{\text{FB}^*} = \frac{K_1P_{\text{FB}}}{1 + K_1P_{\text{FB}} + K_2P_{\text{H}}^{1/2}} \quad (47)
\]

and

\[
\theta_{\text{H}^*} = \frac{K_2^{1/2}P_{\text{H}}^{1/2}}{1 + K_1P_{\text{FB}} + K_2^{1/2}P_{\text{H}}^{1/2}} \quad (48)
\]

Substituting equations (47 and 48) into the rate equation (46) to define the final rate equation (49) in terms of equilibrium constants, partial pressures, and a rate constant.

\[
r = k_3 \frac{K_1P_{\text{FB}}^{1/2}P_{\text{H}}^{1/2}}{(1 + K_1P_{\text{FB}} + K_2^{1/2}P_{\text{H}}^{1/2})^2} \quad (49)
\]

A.2. MATLAB code and fit parameters

The following is an example MATLAB code for model 1B at 85 \( \mu \text{M} \) FB.

\[
\text{This m file is a template to solve for rate constants in a system of nonlinear rate equations. It contains three separate functions to complete this task. They are functions for defining the rate equations (function 3), numerically solving the system of equations (function 2), and optimizing the rate constants to fit the experimental data to the model (function 1).}
\]

In order to better understand the code and what functions are being called upon, it's best to work with the rate equations first (function 3), followed by the ODE solver (function 2), and then the optimizer (function 1).

\[
\text{FUNCTION 1: Optimize the rate constants to minimize the error between}
\]

92
% experimental and modeled data.
function [] = nonlinear_regression()
clc % Clear command window.
clf % Clear current figure.

% Define variables from this function that will be used in other functions.
global Time CB_t CFB_t kapp K1

% FB + _ads ---> FB_ads, rate constant k1
% H + _ads ---> H_ads, rate constant k2
% FB_ads + H_ads ---> B_ads + F_ads, rate constant k3
% F_ads ---> F(aquous) + _ads, rate constant k4
% B_ads ---> B + _ads, rate constant k5

% Experimental times (s)
Time = [0 1500 1800 3600 5400];
% These are the experimentally determined concentrations for species A, B, % and C at the respective times.
% CFB_t = [85.24];
CB_t = [0   2.28    2.32    3.32    4.50];
CFB_t = 85.2 - CB_t;

% Creates a 1x33 vector to use for nlinit.
Cfit = [CFB_t, CB_t];

kapp=0.0000111;
K1=0.0000000029444;
% Initial guesses for rate constant parameters kapp and K1 (see function 3, rateeqns).
beta0 = [kapp,K1];

% nlinit, Nonlinear least-squares regression fitting, minimize the error % between experimental data and the model by optimizing the rate constants. % nlinit follows the form of [BETA,R,J] = nlinit(X,Y,MODELFUN,BETA0). % The outputs beta, R, and J are the vector of optimized parameters, % the residuals, and the Jacobian of modelfun, respectively. % R and J are used to calculate the confidence intervals % on the optimized parameters (below). The first input of nlinit % is the predictor variable, X. However in our case, @modelfun doesn't % use the predictor variable, so it is an empty matrix. The second input, % Y, is a vector of the response variables. These are the experimental data % to compare against the model. The third input is the handle for the % functions containing values for the modeled concentrations. The last term, % beta0, is a vector with the initial guesses for the parameters to be % optimized.

% nlinit works by finding the error between the experimental data and % model using the initial guesses for the rate constants, estimating new % parameters, solving the system of differential equations with the new % estimates, calculating the sum of the squared errors, and continuing to % iterate through that process until the sum of the squared errors is within % the accepted tolerance.
[beta,R,J] = nlinfit([],Cfit,@modelfun,beta0);

%nlparci calculates the confidence intervals of the parameters that
%estimated from nlinfit by using the vector of parameters, beta, the
%residuals, R, and the Jacobian of modelfun.
confint = nlparci(beta,R,J);

%These two commands simply output beta and confint to the command window
%after nlinfit completes its iterations. These values will be the
%optimized rate constants, kapp & K1, with their confidence intervals.
beta
confint
end

%FUNCTION 2: Solve the set of differential equations y' = f(t,y), where the
%vector y represents the concentrations of species A and B. The ODE
%solver in this function calls on the system of differential
%equations, D, from the function rateeqns (function 3). This function requires
%two inputs. The first is the vector of parameters, kapp and K1.
%The values kapp and K1 are defined globally.
%The second input, ~, simply says to ignore the other input arguments.
%This term is necessary because nlinfit can't call modelfun properly
%without two inputs.
function [output] = modelfun(parameters, ~)

%Define variables from this function that will be used in other functions.
global kapp K1 Time CFB_t CB_t

%Defining each component of the input vector, parameters, as a rate
%constant.
kapp = parameters(1);
K1 = parameters(2);

%Create a for loop to obtain the model concentration values corresponding
%to each experimental time point. It will iterate from i = 1 to i =
%the number of components in the Time vector.
for i=1:length(Time)
%Define the initial conditions for the ODE solver. This is a 3x1
%vector.
Uo = [CFB_t(1);CB_t(1)];
%Define the time over which to integrate. ODE solver requires the
%initial time be greater than 0.
tspan = [0.001,Time(i)];

%Solve the set of ODEs defined in the function, rateeqns.
%u is an (x,1) column vector for each time point used in the numerical
%integration. U is an (x,3) matrix, with columns corresponding to the
%concentration of each species and the rows are the concentration at
%each time. The first input to ode23t, @rateeqns, is the function
%handle for the system of differential equations. tspan is the time
period over which to integrate. Uo is the vector with the initial
conditions for the system of differential equations.
\[ t, U = \text{ode23t}(@\text{rateeqns}, \text{tspan}, Uo); \]

length \( U(:,1) \) finds the number of rows in the first column of the U
matrix since the number of time points may vary for each integration.
olength = length(U(:,1)');

These concentrations are the model values at the final time (for each
step in the for loop). With each loop iteration, these row vectors
increase by one column until they are 1x11 vectors. These model
values can now be compared to the experimental values for each
concentration in nlinit.
\[ C_{FB}(i) = U(\text{olength},1); \]
\[ C_{B}(i) = U(\text{olength},2); \]
end

Create a 1x33 vector for input into the least squares fit to minimize
the error with the experimental Ci's.
output=[C_{FB}, C_{B}];

Plot the experimental data and the fits from ODE solver.
figure (1)
errorbar(Time,CB_t,[0 2.74 1.14 5.79 7.04],'go')
hold on
plot(Time,CFB_t,'bo',t,U(:,1),'k',t,U(:,2),'k');
xlabel('Time (s)');
ylabel('Concentration (\mu M)');
legend('CFB','CB','Model 1B');
hold off
axis([0 5500 0 10]);
end

FUNCTION 3: This function defines the rate equations in terms of the rate
constants and concentrations. The inputs to this function are t &
U (defined below). The output is the column vector D (defined below).
function [D] = rateeqns(t,U);
global kapp K1

% FB + _ads ---> FB_ads, eq. constant K1
% H + _ads ---> H_ads, eq. constant K2
% FB_ads + H_ads ---> B_ads + F_ads, rate constant k3
% F_ads ---> F(aqueous) + _ads, eq. constant K4
% B_ads ---> B + _ads, eq. constant K5
% kapp=k3*K1*K2^((1/2)

Defining each component of the input vector, U, as a concentration.
CFB=U(1);
CB=U(2);

Assume elementary reactions, with first order in each species, and
% irreversible.
rate3 = kapp*CFB/((1+CFB*abs(K1))^2);

%D = [dCFB/dt dCB/dt]. These equations define those derivatives in
%terms of the rates of reaction 3.
D(1) = (-rate3);
D(2) = (rate3);
%Transpose the vector from row to column vector for input into the ODE
%solver.
D=D';

end

The MATLAB beta fit parameters were calculated and reported in the workspace for each
model, shown in Table A.1-2, for the lowest and highest FB initial concentrations.

Table A.1. MATLAB beta-fit parameters for [fluorobenzene]₀ of 85 µM.

<table>
<thead>
<tr>
<th></th>
<th>k_{app}</th>
<th>K₁</th>
<th>K₄⁻¹</th>
<th>K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1A</td>
<td>2.53E-2</td>
<td>n/a</td>
<td>1.12</td>
<td>1.78</td>
</tr>
<tr>
<td>Model 1B</td>
<td>1.11E-5</td>
<td>3.59E-10</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Model 2</td>
<td>1.10E-5</td>
<td>n/a</td>
<td>2.885E6</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table A.2. MATLAB beta-fit parameters for [fluorobenzene]₀ of 1.06 mM.

<table>
<thead>
<tr>
<th></th>
<th>k_{app}</th>
<th>K₁</th>
<th>K₄⁻¹</th>
<th>K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1A</td>
<td>0.476</td>
<td>n/a</td>
<td>1.19</td>
<td>140</td>
</tr>
<tr>
<td>Model 1B</td>
<td>0.00021</td>
<td>0.0108</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Model 2</td>
<td>118</td>
<td>n/a</td>
<td>8.13E3</td>
<td>n/a</td>
</tr>
</tbody>
</table>

A.3 H₂ chemisorption and N₂ physisorption

The sample of γ-Al₂O₃ was analyzed via hydrogen chemisorption to determine if there
were any surface sites that formed a bond with hydrogen. Figure A.1 shows that the repeat
analysis point reports a hydrogen uptake less than zero. Likely due to a leak in the connection
from the cell to the instrument manifold when determining the difference in pressure between the
dosed cell and the pressure expected based on the warm free space.
A.4 High-Pressure Liquid Chromatography with UV Detector

There was an initial exploration into using HPLC to detect both product and substrate, due to the aromaticity of the benzene rings the UV detector would have easily been able to detect them at the right wavelength. The HPLC instrument specifications are the following: waters xevo-G2-XS QTOF + H-Class Plus ultra-performance liquid chromatography (UPLC) inlet with an electrospray ionization inlet (ESI) source, quadropole time of flight (QTOF) analyzer, and mass spectrometer (MS) attachment.

The issue of phase separation also played a role in determining which analytical method was appropriate for this system. Working at very small concentrations in the µM range gave us un reproducible data from our calibration standards for benzene with concentrations of 1-50 µM and fluorobenzene with concentrations between 10 - 1000 µM.

Analytical measurements using HPLC were done at the Mass Spectrometry & MS Imaging Center at Columbia University with the assistance of Dr. Fereshteh Zandkarimi. Samples were measured twice between 48-and 168 hours for reproducibility, and a sample would be re-injected and have no visible amount of fluorobenzene standard present. Looking at the literature we speculated that at an appreciable amount of time (t > 24 hours) for the sample to be stagnant, the fluorobenzene substrate in water was separating from the water phase and forming a small fluoros
phase that the injector was plunging through. It was determined from an inability to make a reproducible calibration curve and not having access to the instrument to analyze all materials within a 12-hour window, that this method was not suitable for our analytical kinetics measurements.

A.5. References


B.1. Background

Ten years ago, the United Nations declared access to clean water and sanitation to be a fundamental human right. Since then, scientists have made significant strides in the development of water treatment products; however, work still needs to be done on remediating large classes of highly toxic pollutants, such as dioxins. Dioxins are polychlorinated aromatic compounds, that are the byproduct of such industrial activities as waste incineration, wood combustion, and bleaching. Because these toxins are dispersed through atmospheric emissions and wastewater discharge, they have permeated the water, air, soil, and food chain. Dioxins are linked to a myriad of health problems and diseases including cancer, birth defects, and mental impairment. The natural decomposition of dioxins is slow; without intervention, their accumulation poses a significant health threat to all organic life. The dioxin problem has personal resonance for me. Less than a mile from my residence in Maine is the Indian Island reservation of the Penobscot Nation that continues to suffer from over sixty years of dioxin pollution in their water supply. Industrial polluters, principally the paper mills that formerly used molecular chlorine to whiten paper, poured toxic pollutants into the water some of which remain in the environment. My goal is to use the skills I will develop during my PhD in heterogeneous chemical catalysis to design a low-cost and effective catalyst that selectively dechlorinates dioxin-like compounds to decrease their toxicity and will remain stable under aqueous conditions – a catalyst that could be implemented in the water remediation plant for the Penobscot Nation’s water supply.
B.2. Related work

Existing catalysts, like palladium (Pd) nanoparticles on metal oxide supports, have already demonstrated high selectivity for hydrodechlorination (HDC) of chlorinated alkenes and aromatics under mild conditions.\textsuperscript{80-82} Pd dissociatively adsorbs the hydrogen gas needed to hydrogenate the ring after C-Cl bond cleavage. However, Pd NPs can be poisoned by chloride binding to the surface.\textsuperscript{83} Wong \textit{et al.} synthesized Pd-Au core-shell nanoparticle catalysts supported on carbon (Pd@Au), which increased the dispersion of Pd and decreased catalyst cost.\textsuperscript{80,82} Au weakens the Pd-Cl bond and improves Pd activity.\textsuperscript{80,82-83} A mechanism for the HDC of dichloroethylene over Pd@Au NPs based on data from in situ spectroscopy was proposed.\textsuperscript{82} Surface intermediates were identified, providing evidence to support a mechanism in which HDC happened first followed by hydrogenation.\textsuperscript{82} Reaction mechanisms have been proposed for HDC of chlorinated aromatics on Pd/C under standard conditions, determined by the qualitative formation of products over time.\textsuperscript{81} The HDC rate determining step of chlorinated aromatic species has yet to be determined, limiting catalyst development.

B.3. Proposal

I plan to study the mechanism of HDC of chlorophenols (CPs), used as a model reaction for the remediation of dioxin contaminants in drinking water, catalyzed by Pd@Au/C. CPs serve as simpler model compounds for dioxins that will allow the study of selective C-Cl vs. C-O bond cleavage. To the best of my knowledge, reactions with this bimetallic catalyst have yet to be performed on chlorinated aromatic species. There is a high probability of success using this catalyst because of its performance with aqueous chlorinated alkenes and the success of Pd catalysts in HDC of chlorinated aromatics.\textsuperscript{80-82} Using this model reaction, I aim to confirm the ability of this catalyst to cleave C-Cl or C-O bonds present in dioxins, spectroscopically study the adsorbed surface intermediates in situ, and propose a sequence of elementary steps that explains the observed reaction kinetics. These foundational studies will be combined in a microkinetic
model to elucidate the rate determining step of this reaction, most abundant surface intermediate, dominant reaction pathways, that will then guide the design of an improved catalyst.

B.4. Research plan

Year One: I will synthesize Pd@Au/C catalysts and characterize them using diffraction, photoemission, and electron microscopy. Reaction kinetics measurements of HDC of ortho and meta CPs catalyzed by Pd@Au/C under mild conditions in a plug flow reactor, operating at differential conversion, will determine product formation as a function of varying space velocities. Based on results published for Pd/C, I anticipate that selective cleavage of the C-Cl bond will be observed under these reaction conditions.\(^{76}\) I will propose a reaction pathway based on the results of these studies coupled with the knowledge of observed reaction products. It is imperative that I further develop mechanistic information, using in situ spectroscopy, to optimize the selective HDC of dioxin-like pollutants.

Year Two: Under aqueous conditions, in situ spectral analysis using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) will be used to measure the vibrations of adsorbed surface species. Potential observed surface species include chlorophenol, chlorobenzene, phenol, benzene, and cyclohexane. These surface species have been observed spectroscopically and can be distinguished with ATR-FTIR.\(^{84}\) From this spectroscopic study, abundant surface intermediates will be identified. Furthermore, developing a more robust reaction pathway requires asserting a series of elementary steps which must include the observed abundant surface species intermediates.

Year Three: By combining theory and experiment, I will gain insight into the fundamental performance of the catalyst under relevant reaction conditions. I will use density functional theory (DFT) to calculate binding energies and estimate activation energy barriers from scaling relations. DFT calculations will provide insight into tuning the activation energy barriers. A microkinetic
model will define the rate limiting step of this reaction pathway and further advance the development of a practical industrial catalyst for water purification.

B.5. Impact of results

My findings will be presented to regional and national catalysis communities and published in peer-review journals. Detailed highly technical studies have relevant applications in interdisciplinary areas of engineering design. My work will contribute to the design and implementation of the most efficient low-cost HDC catalyst for water treatment remediation of dioxins that can be implemented on a global scale.

B.6. Intellectual merit

Although water pollution remains a major scientific and technical problem, no effective, low-cost catalysts have been developed to break down dioxins, a major source of industrial pollution. This work would lead to a better understanding of the mechanisms underlying dioxin breakdown and interactions with major classes of catalysts, leading to the development of new catalysts with major applications to industry, ecosystem rebuilding, and marginalized global communities’ access to clean water. My work will contribute first steps to establishing a comprehensive understanding of the fundamental science of dechlorination catalysis that will inform related areas of hydrodehalogenation catalysis. The University of Maine at Orono, where I am currently a graduate student, is an ideal place to carry out my research. The university has a working relationship with leaders of the Penobscot Nation, and has laboratory facilities in areas of surface science, catalyst characterization, and reactor development for heterogeneous catalyst systems, both vital for water treatment explorations. In addition, high-resolution transmission electron microscopy facilities at Columbia University have been made available to me through my dissertation committee member, Dr. Rachel Narehood Austin.
B.7. Broader impacts

The pollution of drinking water affects millions of people across the United States, particularly marginalized communities living adjacent to waste sources. This work will lead to the development of catalysts capable of breaking down dioxin pollutants. I am motivated to make substantial and lasting impacts on water purification. To disseminate the results of my research to the broader community, I will also create a learning module to be used in the Indian Island school to help educate younger generations on how knowledge of chemistry and chemical processes can be used as a tool for social justice. I will continue to use science as a tool for social and environmental activism, and I aim to inspire scientists, engineers, and science communicators to invest their research efforts in areas that improve the quality of life for communities that have limited resources or have been systematically ignored.

B.8. References


Appendix C

CHEMISTRY AND RACISM:

SUPPLEMENTAL INFORMATION

Chemistry and Racism: A special topics course for students taking general chemistry at Barnard College in Fall 2020
Lauren Babb¹, Rachel Narehood Austin²*

¹ Department of Chemistry, University of Maine, Orono ME
² Department of Chemistry, Barnard College, 3009 Broadway NY NY 10027

In the supplemental material, we provide the following:
1. The description of the course as it appeared in the course catalog.
2. A summary of the end of semester evaluation of the special topics course.
3. A table that includes the student generated discussion questions.
4. A copy of the syllabus.
5. A copy of the letter written by students and alums, shared with their permission, but with their names removed.

C.1. Description of special topics courses in the Barnard Course Catalog

CHEM BC1004 Special Topics in Chemistry is designed to give students the opportunity to explore their interests in chemistry while simultaneously taking CHEM BC2001, General Chemistry lecture and lab. Only students currently enrolled in CHEM BC2001 are eligible to take the course and students must select one of the FIVE topics. The topics included are: MONDAY Chemistry and Racism, TUESDAY The Chemistry of Color, WEDNESDAY The Chemistry of Covid-19, THURSDAY An Introduction to Chemical Engineering, FRIDAY The Chemistry of Lead. Students who have previously taken CHEM BC2001 may enroll with special permission of the instructor but priority will be given to current CHEM BC2001 students.

C.2. Summary of Teaching Evaluations for CHEMBC1004 Special Topics in Chemistry: Chemistry and Racism

This course was evaluated using the standard course evaluation instrument provided by Barnard College and Columbia University.

The evaluation asks the following questions:
1. How would you rate the overall quality of the course?
2. How would you rate the clarity of course objectives?
3. How would you rate the organization of the course?
4. How would you rate the clarity of course requirements?
5. How would you rate the clarity of grading standards?
6. How would you rate the extent to which class began and ended on time?
7. How would you rate the overall quality of the instructor's teaching?
8. How would you rate the instructor's effectiveness in communicating the subject matter?
9. How would you rate the instructor's ability to stimulate your intellectual curiosity?
10. How would you rate the instructor's ability to stimulate student participation in class?
11. How would you rate the instructor's effectiveness in answering questions?
12. How would you rate the instructor's feedback on your work?
13. How would you rate the instructor's timeliness in returning your work?
14. How would you rate the instructor's availability during scheduled office hours?
15. How would you rate the adequacy of scheduled office hours?
16. How much has the course increased your interest in the field?
17. How much has the course increased your understanding of the broader intellectual field?
18. How much has the course improved your quantitative skills?
19. How much has the course improved your presentation skills?
20. How much has the course improved your writing skills?

Students are required to submit these evaluations in order to access their grades quickly. Students are asked to use a 1-5 ranking, where 1 = not at all, 2 = very little, 3 = some, 4 = quite a bit, 5 = very much.

Faculty are provided with the median and standard deviation for their class and also the mean and standard deviation for their department and the college.

Note that the special topics courses were the only courses the chemistry department offered in the Fall A block and so course and department averages are very similar.

In addition, students are asked the following free response questions.

1. Why did you take this course?
2. What did you value most about this course? In what ways did the course meet your expectations? Explain why you would or would not recommend this course?
3. What improvements would you like to see in the organization and content of the course?
4. Did the course inspire you to put in extra time and effort, over and beyond what was required? Can you explain why or why not?
5. What did you value most about your instructor's teaching methods?
6. What improvements in the instructor's teaching would you recommend?

Overall students were very positive about the course with the mean being above the department and the college for all questions except for question 17 where the response was very similar to the department average and questions 18-20, which were unrelated to the course aims.
At A Glance : Course Overview

| Q1-1 | How would you rate this course on the following dimensions? The overall quality of the course |
| Q1-2 | How would you rate this course on the following dimensions? The clarity of course objectives |
| Q1-3 | How would you rate this course on the following dimensions? The organization of the course |
| Q1-4 | How would you rate this course on the following dimensions? The clarity of course requirements |
| Q1-5 | How would you rate this course on the following dimensions? The clarity of grading standards |
| Q1-6 | How would you rate this course on the following dimensions? The extent to which the class began and ended on time |

At A Glance : Instructor Overview

| Q7-1 | How would you rate your instructor in the following areas? The overall quality of the instructor's teaching |
| Q7-2 | How would you rate your instructor in the following areas? The instructor's effectiveness in communicating the subject matter |
| Q7-3 | How would you rate your instructor in the following areas? The instructor's ability to stimulate your intellectual curiosity |
| Q7-4 | How would you rate your instructor in the following areas? The instructor's ability to stimulate student participation in class |
| Q7-5 | How would you rate your instructor in the following areas? The instructor's effectiveness in answering questions |
| Q7-6 | How would you rate your instructor in the following areas? The instructor's feedback on your work |
| Q7-7 | How would you rate your instructor in the following areas? The instructor's timeliness in returning your work |
| Q7-8 | How would you rate your instructor in the following areas? The instructor's availability during scheduled office hours |
| Q7-9 | How would you rate your instructor in the following areas? The adequacy of scheduled office hours |

At A Glance : Student Growth

| Q2-1 | How much has this course enabled you to do each of the following? Increase your interest in the field |
| Q2-2 | How much has this course enabled you to do each of the following? Increase your understanding of the broader intellectual field |
| Q2-3 | How much has this course enabled you to do each of the following? Improve your quantitative skills |
| Q2-4 | How much has this course enabled you to do each of the following? Improve your presentation skills |
| Q2-5 | How much has this course enabled you to do each of the following? Improve your writing skills |
### C.3. Student generated discussion questions

#### Table C.1. Student-generated discussion questions

<table>
<thead>
<tr>
<th>Class topic</th>
<th>Discussion questions</th>
</tr>
</thead>
</table>
| **Representation in chemistry departments in the US** | 1. How does a lack of diversity in the faculty affects our education?  
2. How does it change what we are taught curriculum-wise?  
3. How does it change our attitudes towards others in the STEM fields?  
4. What would we gain from more diverse teachers?  
5. How do we see structural racism manifest itself when it comes to institutional/grant funding?  
6. How can institutions and grant programs change their practices to combat their observed structural racism? |
| **Voices and histories of Black American chemists** | **TOKENISM**  
How do we distinguish between actually making progress in the hiring process and just trying to fill a quota?  
What can non-Black students and administrators do in the meantime to make Black students feel more included and not tokenized?  

**ACADEMIA**  
How can we make it so Black people can continue doing what they love and simultaneously feel like they have a space in that world?  
How do we change the fact that Black professionals are forced to work for other communities and not their own? How do we see this in both academia and in industry?  

**INTERSECTIONALITY**  
How do we promote Black women into the academia of chemistry?  
What role can social media play in empowering Black professionals?  
***ALICE BALL DAY IS LEAP DAY***  

**RESPONSIBILITY**  
How do we move the responsibility of including Black people in STEM away from Black people themselves to non-Black people and administration?  
How do we take the responsibility off of Black students in STEM to be the face of all Black students in STEM? |
| **Reconstructing organizations to create change** | How can we work to ensure that any changes we make to expand our inclusivity at Barnard are actually long-lasting and maintainable? Is there room to create a space within the Barnard curriculum to educate students about the often-ignored experiences of Black people in the classroom and workplace without it being a burden on Black students to be educating their peers (unless something like this exists already)?  
How can we ensure a constant (or consistent) state of engagement with the inclusion and diversity of our institution, so we do not only address issues of inequality/inequity as they come in?  
In the working environment, in what ways can we make the inclusive events meaningful, not superficial? And how can we make sure that it is "effective"?  
The HBR article talks about employers making sure not to unfairly overburden employees.  
How do certain kinds of class assignments place unequal burdens on students?  
How can we reconsider assessments of student performance to ensure that |
everyone is challenged and receives helpful feedback without glorifying a “stress culture” or overburdening Black and BIPOC students?
Is there any way that we can offer enough financial support to the underprivileged students (e.g. fundraising events like Dana-Farber marathon challenge)?

Last week we mentioned the introductory science courses that intend to “weed out” students who will not continue on to higher paths of STEM education, which is related to how a professor or teacher understands ability and talent.
What are different ways we can view these classes (in terms of knowledge and ability growth) and how can we encourage professors to advertise their classes in different ways?
Are there ways our curricula would have to change in order to accommodate a growth mindset model?
How would we evaluate the faculty’s perceptions of potential in students? Would it be ethical to check their perceptions?

| Recommendations to Barnard College – discuss options | Should a class similar to this one be required at Columbia/Barnard for those taking a STEM course for each specific department (biology and racism, etc) that addresses racist origins and aspects of the subject today? And should a class like this be offered/required for non-STEM majors?
How should intro classes be reformed in order to create more inclusive and anti-racist environment?
How can these forums be implemented in a non-performative way?
Should the class “chemical problem solving” be open to students who have already taken AP chemistry?
How can we encourage Columbia to follow in our steps? |
|---|---|

C.4. Syllabus from Chemistry and Racism: A Special Topics Course

**CHEM BC1004**
Special Topics: Chemistry and Racism Fall 2020

**Course times**
M 10:00-10:50 am

**Course text/materials**
Text: There is no text for the class. All readings and videos will be on our courseworks page

**Other materials:** You will need a computer on which to connect to the class via Zoom

**Course description**

BC31004 Special Topics in Chemistry: Chemistry and Racism is a 0.5-point course offered in both block A and block B in fall 2020 to create an intellectual community where we can discuss connections between chemistry and other topics of interest. Students enrolled in the class will have an opportunity to examine racism in the context of chemistry and to help the Barnard Chemistry Department develop and implement antiracism policies and projects.

**Learning objectives**

Students who successfully complete this course will demonstrate:
• a thoughtful perspective on how to affect change to make society and our community less racist;
• an in-depth understanding or appreciation of a topic of the student's choice;
• a willingness to engage in discussion with peers

Course prerequisites/corequisites

There are no course prerequisites. Students must be currently enrolled in BC CHEM 2001.

Course website

The website can be accessed through Columbia Courseworks (https://courseworks.columbia.edu) and will contain all materials pertaining to this class.

In class discussions

We will meet via Zoom. If students live in a time zone where synchronous participation is not possible, please make arrangements with the instructor. To the extent that there are small presentations, those will be recorded but class discussion will not.

Out of class discussions

Students can use the discussion forum for out of class discussion.

Grading Overview

This class will be graded in the P/D/F format. Students who attend every class and submit a weekly response to the weekly writing prompt and who participate in our final project will pass the course. Students who miss classes but still complete the weekly responses to the writing prompts will also pass the course.

Project

The project I've set for us is to develop a set of anti-racist policies and activities for the chemistry department and to develop a plan for implementation and evaluation. There are many stakeholders with interest in this project and much to learn about what we have already done and what the best practices are. It is likely that we won't finish the entire project in 6 weeks, but we will make progress and we have two sections of this course so hopefully by the end of the fall semester, we'll have a list of actionable items and we'll begin "actioning" them. In some cases, we may want to work with other STEM departments to develop STEM-wide practices.

Class attendance and participation

The best thing you can do is attend every class and stay focused (there are only 6). We will select students to lead class discussion after the first class. Class discussion leaders will manage the class discussion and call on people to speak. They should also come prepared with questions on the reading.
Electronic devices

I realize that because we will use computers to connect to this in class, it makes it more tempting for you to use those devices to multitask – like checking email or viewing text messages or any other sort of non-academic social media involvement. I strongly encourage you not to do this and to instead focus on the class during the class time. Being able to stay focused on class is something that will help make the semester more rewarding (I speak from experience on this point).

Recording class, audio and/or video, is not permitted, without instructor permission.

Honor code:
Every student who registers at Barnard agrees to maintain the following Honor Code (established in 1912 and revised in 2016):

We, the students of Barnard College, resolve to uphold the honor of the College by engaging with integrity in all of our academic pursuits. We affirm that academic integrity is the honorable creation and presentation of our own work. We acknowledge that it is our responsibility to seek clarification of proper forms of collaboration and use of academic resources in all assignments or exams. We consider academic integrity to include the proper use and care for all print, electronic, or other academic resources. We will respect the rights of others to engage in pursuit of learning in order to uphold our commitment to honor. We pledge to do all that is in our power to create a spirit of honesty and honor for its own sake.

Barnard students reaffirm their acceptance of the Honor Code each year by signing their registration forms. Columbia students commit themselves to the Honor Code upon registering for a Barnard course.

Community statement: “All students are expected to conduct themselves in a manner compatible with the College’s mission as an educational institution and a community of students, scholars, and teachers. Common goals are to protect and respect each individual’s well-being and to enable us to live and work together with a minimum of conflict and a maximum of personal freedom. It is the right of each member of our community to attend, make use of, and enjoy the facilities and functions of the College without interference or disruption. Students’ failure to comply with these standards of conduct may result in discipline.”

Medical schools only accept students who have demonstrated that they treat others respectfully. We are particularly sensitive to ensuring that faculty, staff members, and other students are, at all times, spoken to politely. Some of you are likely to ask faculty associated with general chemistry for letters of recommendations. The students who are easiest to write strong letters of recommendations for are students who comply with these standards of conduct and who work hard, are intellectually inquisitive and honest. The final grade you receive in general chemistry is only one factor among many that determine whether we can provide letters that help you with your academic career.

We look forward to maintaining a respectful supportive learning community this semester.

Center for Accessibility Resources & Disability Services: Students in this course who may need disability-related accommodations should let me know by the end of the second week of the semester. Students who need test or classroom accommodations must be registered in advance.
with the Center for Accessibility Resources & Disability Services (CARDS) in 008 Milbank (https://hood.accessiblelearning.com/Barnard/, 212-854-4634). Students must register every semester to be eligible. Please note that the chemistry department does not have the ability to offer examination with extended time so all students with diagnosed accommodations will schedule their exams with CARDS. Students with accommodations are strongly encouraged to use them. Often students wait until after the first or second examination to realize that learning differences that they dealt with in high school continue to affect their performance. We recommend that you err on the side of caution in electing whether to utilize an available accommodation. I am happy to answer questions about learning differences.

**The Barnard College wellness statement**: “It is important for undergraduate students to recognize and identify the different pressures, burdens, and stressors you may be facing, whether personal, emotional, physical, financial, mental, or academic. We as a community urge you to make yourself – your own health, sanity, and wellness – your priority throughout this term and your career here. Sleep, exercise, and eating well can all be part of a healthy regimen to cope with stress. Resources exist to support you in several sectors of your life, and we encourage you to make use of them.”

Learning to manage stress is an essential life skill. I encourage you as a community of scholars to focus on talking about the beauty of science and its power to explain interesting phenomena and the privilege you may someday have to help alleviate human suffering or to advance human knowledge and to not discuss grades or grade-related anxiety in ways that simply exacerbate stress.
C.5. A Letter to the Barnard College Chemistry Department from Alumnae

Dear Barnard Chemistry Department,

A month ago, a letter was sent to the Barnard Chemistry Department listserv affirming the Chemistry department’s (and other Barnard STEM departments’) support of Black Lives Matter and to “reaffirm [its] commitment to Barnard’s Diversity Mission statement.” A recent letter from Barnard Black alumni as well as a petition from numerous STEM students have demanded revisions to the Barnard curricula that would be a first step to interrogating the anti-Blackness and racism embedded in STEM and in Barnard’s history.

These two letters -- and in particular the letter and efforts from Black alumni -- have served as a call to action for us, those signed below. As students we are contributing members of the Barnard institution (both in monetary ways and also in our time and labor) and as such validate, to some degree, Barnard’s broader actions. We recognize the active role this community has in the gentrification of the Morningside Heights and Harlem neighborhoods. We acknowledge the way in which academia was historically built to further white men and white supremacy and to exclude non-white and low-income peoples. We are conscious of Barnard’s history and founding as an institution for wealthy white cis-women and its historical exclusion of underrepresented people including Black and Brown folks, those with lower incomes, and trans and non-binary people and the continued ways in which these underrepresented peoples are marginalized on our campus. Most importantly, we are cognizant that our participation as students at Barnard helps sustain the structures that allow white supremacy to continue.

We write this letter not as representatives of the Chemistry student or alumni body but as a group of students deeply impacted by these recent events. We hope these ideas, thoughts, and questions will invite further collaboration on changes within the department. We believe that the Chemistry department must become a force for change in an overall mission of creating an anti-racist Barnard and we hope that this letter will allow us to work together to achieve such a goal.

Our asks:

1. We ask that the Chemistry department present and commit to a plan to increase the percentage of faculty with underrepresented identities, in particular Black and Indigenous faculty, over the course of the next few years. We also ask that the department support such faculty in gaining tenure with the goal of increasing the number of tenured faculty with underrepresented identities. Such a plan should be made public and available to students, in particular the strategies for attracting, retaining, and supporting applicants with underrepresented identities. The Chemistry department should also present a public statement of their support for faculty from underrepresented identities.

2. In the spirit of collaborative work and in recognition that creating a truly anti-racist curricula requires time, we want to suggest creating a paid student committee to work alongside the department. Such a committee would serve as a liaison between students and faculty, allowing for the department to get a better sense of student interests and for students to provide input on the curriculum. Ultimately, we hope such a committee would help hold both students and faculty accountable in creating and reinforcing an anti-racist department.

3. We also discussed the extension and formalization of a department facilitated lending system for chemistry materials. While the Barnard FLP library is a resource for textbooks, at the moment, there is no formal lending system for model kits, calculators, or other chemistry materials. We propose
formalizing a lending system that is well advertised and available to any student taking a chemistry course. Such a system would allow students to “check out” materials for the duration of the course. We also suggest actively encouraging students to donate their model kits and calculators at the end of the semester. Providing such materials would lower the financial barrier to actively participating in chemistry courses and the department. Furthermore, we encourage exploring course material options (for textbooks and online programs such as Sapling) that lower the financial barrier to chemistry.

(4) We want to encourage the implementation of a regular and mandatory anti-racism training for students and faculty in the department. Just as lab safety training is necessary to ensure the health of everyone in the lab, anti-racism training is imperative to unlearn harmful practices and ensure the welfare of our community. Such training will create a safer community for not only students, but also faculty and staff.

(5) We propose the creation of a formalized anonymous reporting system (with transparent protocols for handling reports) for discriminatory or harmful acts available to both students and faculty. A formalized system provides students and faculty with the knowledge that should anything ever happen, there is a clear process on how to report discriminatory acts and, more importantly, clarity on how a report would be handled and addressed. Such a system should be made available to faculty as well because we recognize that students can also be complicit in creating an unhealthy and harmful atmosphere. We spent a lot of time discussing and debating the best way to set up such a system and as such, recognize the complexities in doing so. Therefore, we look forward to explaining more of our ideas through discussion rather than in this letter.

In addition to these ideas, we also spent quite a bit of time discussing our own experiences with the department, broader and more amorphous changes we would wish to see, and questions we had about the department. In our conversation we continually returned to a question of flexibility in chemistry. We brought up personal concerns surrounding the intensity of the major course load and the lack of flexibility that students have in selecting courses that are most appropriate for their chemistry background. We also touched upon the difficulty students have encountered with making up labs, exams, or assignments. Ultimately, we settled on two related core questions that we feel best encapsulate our feelings: Who is the chemistry department for and what do the chemistry/biochemistry majors prepare us for? These questions encompasses a number of our concerns such as:

- **Past chemistry/science background** - The chemistry major and the introductory chemistry track in particular is often presented as a “one size fits all” for students regardless of past background. We wondered how we might present more support and alternatives for students who may feel less confident in their chemistry knowledge. One recommendation was to better advertise the Chemical Problem Solving class and actively work to reduce any and all stigma attached to the class, which we recognize has already been happening.

- **Career paths** - We felt that the chemistry major encourages a student to obtain a higher degree (such as a masters or PhD) and enter academia. While we recognize the merit in encouraging students to follow such a path, we also want to acknowledge that academia is deeply exclusionary and racist. What does it mean for this department to encourage students to enter a field that cannot sustain them, especially without recognizing the hostility? How might we expose and examine the way in which academia was built for cis-white patriarchy and supremacy both through formal classes and
extracurricular lectures? How can we encourage students to explore other career paths in addition to academia, while also reshaping academia to be more inclusive?

- **Community care** - We also considered how important the professors, the instructors, and the TAs have been to our Barnard chemistry experience. Students are also capable of acting in harmful ways against faculty, whether intentionally or not, and we wanted to find a way to both protect faculty from harm and hold such students accountable for their actions.

We have many more disparate thoughts that we felt would be better relayed through conversation rather than a letter and we are sure that the broader chemistry student body will have more to say. However, we hope that this letter might serve as a general overview of our thoughts, perspectives, and concerns about the Chemistry department and that it might open up a path for broader dialogue and collaboration across the department. We are eager to engage with you about these questions and work together to find solutions. Recognizing that we are just a few of the students engaging with the Chemistry department and that we each have specific and personal identities, we ask that this broader dialogue be advertised to and open to any person who has taught or taken a chemistry course through an email to the department and Barnard Chemical Society listserv, and alumni of the department. We look forward to hearing from you soon.

Best,
Kalina Ko ‘21
Erika Amemiya ‘21
Isabel Klein ‘18
Frieda Muller, ’22
Juliet Lee ‘21
Natasha Reich ‘21
Liz Irvin ’21
Maria Paley ’17

**Resources:** These are some resources that we have been learning from and have used in writing this letter.

- #STEMforBLM Resource List
- Black Scientists Call Out Racism In Their Institutions
- Columbia People’s COVID Response and the linked guide to Columbia Gentrification created by CAGe
- Empowering women of color to succeed in STEM
- Black girls who code
- SACNAS Conference
- Fight the Tower
C.6. Black Alumnae Letter to Barnard Leadership: June 20, 2020
June 22, 2020

Dear Barnard Trustees, President Beilock, Provost Bell, and Administrators,

In the midst of a global health crisis and uprisings around anti-Black violence, we write this letter as a response to our white and non-Black alumnae allies reflecting on the inequities and racism they’ve witnessed. They were curious to hear our stories. Thus, we communicated a call to our community: who will join us in amplifying our voices? In just a span of a few days, we have seen hundreds of Barnard students and alums across multiethnic and intergenerational identities look to hold the institution accountable, in order to defend Black lives.

As Black Barnard alumnae, we stand in the legacy of Zora Neale Hurston ’28, who was not allowed to live in Barnard dormitories as a student, yet is now celebrated as one of the College’s most notable alumnae. We know the feelings of being silenced, excluded, and overlooked, yet staged to promote diversity to prospective students and the public. There are countless other Black alumnae, ourselves included, whose experiences were fraught with racism, microaggressions, and eventually disenchantment, for a place that positions itself as an “institution that aims to interrogate racism and systematic discrimination in all its forms and to produce knowledge and actions that help address entrenched disparities in our society.” - Letter from President Beilock

We are pushing this institution past band-aid practices such as task forces, listening sessions, and penned letters that often read as performative. When will the marginalized students, alumnae, staff, and faculty stop bearing the burden of creation and advocacy at Barnard? The data, stories, and pain exist and you are well aware of the work that needs to be done.

The following asks have been thoughtfully informed and prepared by Black alumnae and current students across class years, as well as alumnae who attended a virtual Town Hall on June 12, 2020. In the vein of immediate and urgent action, we offer the following solutions for administrative priority:

1. By the end of next FY 2020-2021, the office of Public Safety must be re-structured and reimagined with input from current students, faculty, and staff. We ask that these new plans be made transparent in a public forum, in which alumnae can participate.
   a. The creation of the Barnard Community Safety Group, which was formed after the 2019 physical restraint of Alexander McNab, is not a strong enough response. We echo the words of the VP of Diversity, Equity, and Inclusion, Ariana Gonzalez Stokas, who shared that “for many on campus, this incident symbolized the persistent anti-Blackness of policing.” -The Work of Racial Justice

2. Starting in the fall of 2020, all trustees, faculty, staff, and incoming first-year students must participate in mandatory anti-racism training, rooted in challenging privilege, oppression, and power. We expect this training to be facilitated by Black professionals who are certified and well versed with intersecting identities. These models exist for similar training across the College i.e. “Consent is Sexy” (New Student Orientation Program).

3. Starting in the fall of 2020, the College must provide full transparency and clarity around staff, faculty, and administrators’ demographics and turnover across campus. The recent and inconspicuous elimination of two Black women Vice Presidents of Communications and Human Resources, respectfully, has highlighted that Barnard must track and release this data.
   a. A public report must be published annually and provide answers not limited to the following questions:
4. Starting in FY 2021-2022, a hiring requirement to honor employees from the Harlem community across all levels, especially in executive positions, must be implemented and advised on by the VP of Diversity, Equity, and Inclusion.

5. As a follow up from the Diversity & Inclusion Task Force, the College must implement the recommendation of “adding up to 10 additional faculty of color to our tenured and tenure-track ranks.”
   a. Since the recommendations were published in 2017, how many of these positions have been filled? As referenced again in: New Initiatives Launched on Diversity and Inclusion
   b. If little progress has been made, we strongly suggest that half of these ranks be filled by Black faculty. We want to see Black faculty hired across disciplines beyond the humanities, such as in STEM.

6. Starting in the fall of 2021, the VP for Diversity, Equity, and Inclusion, Ariana González Stokas, must have an expansive budget allocated to her office that supports her initiatives as well as the opportunity to expand her staff.
   a. The College must push beyond tokenizing women of color by placing them in leadership positions that put the onus on them to solve anti-blackness and discrimination. Diversity, equity, and inclusion must be campus wide initiatives that have buy-in from all constituencies, including senior staff, the President, and trustees.

7. Starting in the fall of 2021, Black History, Critical Race Theory, and Ethnic Studies must be central to the Foundations curriculum. Barnard must reckon with its own deep anti-black history through academic and campus wide initiatives.
   a. While Barnard prides itself on a versatile and expansive curriculum, the “Thinking about Social Difference” mode of thinking addresses some of these issues, but still allows for a level of disengagement with these topics.
   b. Foundations must be revised to emphasize Black history and the histories of Indigenous, Latinx, Asian, Pacific Islander, Middle Eastern, LGBTQ, undocumented, and disabled people through an intersectional lens.

As a predominately white and affluent institution, Barnard must take an active commitment against anti-Blackness. The time is now. Our lived experiences prove that one hundred and thirty one years since its founding, Barnard continues to perpetuate ideals and practices that center the experiences of affluent white cisgender women.

Barnard taught us how to interrogate systems and question the histories that inform our current moment. With students and hundreds of alumnae in solidarity with us, we expect that our solutions are met with open-mindedness and a willingness to reimagine how this institution can serve us, your Black students and alumnae. We write this letter with the intention of mobilizing and empowering fellow alumnae to call Barnard to action. We look forward to your prompt response.

Sincerely,

Cinneah El-Amin BC’16, incoming Chair of Young Alumnae Committee (AABC), Board Member for Black Alumni Council of Columbia University, Senior Marshal, Bear Pin recipient
Naintara Ramoo-Goodgame BC’15, Board Member for Black Alumni Council of Columbia University, Senior SGA Leadership Award recipient
Marquita Amoah BC’16, former member of Office of the President and Office of Admissions, Senior SGA Leadership Award recipient, Senior Marshal
BIOGRAPHY OF THE AUTHOR

Lauren Olivia Babb was born in Summit, New Jersey on August 27, 1996, to Dr. John and Lareen Babb. She grew up in Watchung, New Jersey with her younger sister Rebecca and their two dogs Luke and Ruby. At 18 years of age, Lauren started at Barnard College of Columbia University in the City of New York where she received a B.A. in Chemical Physics. Lauren was the first Black/African American woman to complete this undergraduate degree program. Lauren was accepted in a Physics Ph.D. program at the Université Libre des Bruxelles but decided not to matriculate in Fall 2018. Instead, Lauren went back to conduct heterogeneous catalysis research in the Austin Lab at Barnard College while applying to graduate programs in the U.S. Lauren began her studies at The University of Maine in 2019. Lauren became a mother to a feisty long-haired dachshund, Velma, born June 27, 2021. Lauren and Velma are excited to move back to the tri-state and begin a career in analytical environmental science and technology. She is a candidate for the Master of Science degree in Chemistry from The University of Maine in August 2022.