

Synthesis of a catalyst for renewable fuel production

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Atmospheric carbon dioxide levels have been on the rise for decades as the combustion of fossil fuels, such as natural gas and coal, has become increasingly prevalent³. CO₂ traps heat in the atmosphere, a phenomenon known as the 'greenhouse gas effect' which is the driving force behind global climate warming. The Tate lab aims to mitigate CO₂-induced warming by applying chemical catalysis to the production of sustainable fuels. Hydrogen gas (H₂), which has been studied extensively as a renewable fuel, has demonstrated too low of an energy density for use in transportation, and other practical contexts. Instead, we aim to synthesize a catalyst that combines H₂ with CO₂ to form a fuel with high energy density (e.g., formic acid). Using CO₂ as a feedstock for fuel production allows us to recycle it after combustion, rather than release it into the atmosphere.

Catalysts are necessary to cleave H₂ into a proton (positively charged hydrogen atom) and hydride (negatively charged hydrogen atom), which consequently allows for hydrogenation of CO₂. The fundamental composition and structure of our catalyst relies upon the Hard Soft Acid Base Theory (HSAB). HSAB, which is based on the well-known Lewis theory of acids and bases, describes how soft acids (i.e., copper, silver, and gold) would rather bond to soft bases due to their covalent bonding preference, and hard acids would rather bond to hard bases (i.e., alkoxides) due to their preference for ionic bonding. Our strategy for catalyst design involves mismatching soft acids with hard bases. We hypothesize the hard-soft mismatch will cleave H₂ to form a soft acid – hydride complex, and hard base – proton complex suitable for the hydrogenation of CO₂ and the formation of energy-dense products.

I spent much of my time this summer synthesizing N-heterocyclic carbenes (NHCs): ligands that stabilize our soft acids and donate electrons into their orbitals. NHCs contain a central ring of varying sizes; we mainly attempted to synthesize 5, 6, and 7-membered rings. Additionally, the ligand's bulky substituents have a shielding effect on the soft acid. The synthesis of NHCs involves two consecutive procedures. The first, which forms a formamidine (a molecule similar to an NHC, but without the completed central ring), takes approximately two days. Whereas the second step, which synthesizes the complete NHC (also known as an amidinium), takes an additional day^{1,2}. This summer, I successfully synthesized 6 and 7-membered ring NHCs with mesityl (Mes) and diisopropyl (Dipp) substituents. The Tate lab primarily uses proton nuclear magnetic resonance (¹H NMR) spectroscopy to verify the structure of our product and determine the results of our experiments. According to the NMR data, our attempts at synthesizing 5-membered ring NHCs for the Mes (5Mes) and Dipp (5Dipp) series were unsuccessful, as both NMR spectra displayed large impurities. However, we were able to successfully prepare 6 and 7-membered NHC ligands with bulky substituents.

I followed up these results by pairing Mes NHCs with soft acids (primarily silver and gold) and hard bases (alkoxides). The ¹H NMR spectra of the 6-membered ring Mes NHC (6Mes) silver bromide (AgBr) complexes showed that I had synthesized the homoleptic, rather than heteroleptic product; meaning that two 6Mes molecules had bonded to the silver, rather than one. The homoleptic product is problematic, as we need the alkoxide to bond to the silver as well. I was successful in preparing a complex of 7Mes with gold chloride (AuCl); however, when the alkoxide was added, the ¹H NMR spectrum showed significant impurities. Based on these results, we decided to shift our focus to NHC ligands that prefer other soft acids, narrowing the focus of the lab's efforts on more promising mismatched acid-base pairs.

I would like to thank the Kufe Family Research Fellowship for providing me with the funds necessary to engage in this fantastic academic opportunity. As an anthropology major, I'm most interested in how human beings interact with a rapidly changing environment. My summer research experience in the Bowdoin Chemistry Department showed me how humans utilize scientific knowledge to adapt to their surroundings, whether that be through environmental chemistry, or other fields.

Faculty Mentor: Dr. Brandon Tate

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