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Project Title: Selective Hydrogenolysis of C-Cl Bonds: A Fundamental Reaction Kinetics Study

PI: Thomas J. Schwartz, Chemical & Biomedical Engineering, University of Maine

Impact of the Research

The selective hydrogenolysis of carbon-X bonds, where X can be a carbon, oxygen, nitrogen, sulfur, or a halide such as chlorine, is an important class of reactions in the production of chemicals from petroleum feedstocks. In particular, the synthesis of certain chlorobenzenes and chlorophenols from benzene and phenol, respectively, involves the selective hydrodechlorination of polychlorinated species.¹⁻² This reaction is attractive not only because it provides a use for unwanted byproducts (*i.e.*, over-chlorinated benzenes or phenols) but also because it can provide access to certain isomers not obtainable by other means (*e.g.*, species chlorinated in the *meta* position). While much of the research in the petrochemical field has historically focused on the cleavage of C-C and C-N bonds, the cleavage of C-Cl bonds shares many features with these better-studied reactions. According to Sinfelt, the hydrogenolysis of ethane, methylamine, and methyl chloride all proceed by a similar mechanism, shown in Sequence 1,³ and in all three cases, the rate-controlling step in the reaction is the cleavage of the C-X bond.

Inspired by the lack of fundamental, molecular-level insights into the hydrogenolysis of carbon-chlorine bonds in aromatic systems, this project aims to study this reaction in detail. Such understanding is imperative for the design of new catalytic materials. Our research objectives focus on elucidating the reaction kinetics and mechanism for C-Cl hydrogenolysis using two common catalysts: Pd and Ni. Discrepancies in the reaction kinetics data presented in the literature suggest that this reaction may occur by a different mechanism over each catalytic material; although such a difference would be in contrast to the observations of Sinfelt for hydrogenolysis reactions in general.⁴

We hypothesize that the hydrogenolysis mechanism should actually be equivalent for both Pd and Ni, and we are undertaking to test this hypothesis by combining classical reaction kinetics measurements, isotopically labeled experiments, and *in situ* Fourier transform infrared (FTIR) studies.

Sequence 1: Hydrogenolysis of methyl chloride

1. $H_3C-Cl + 2^* \rightarrow CH_3^* + Cl^*$ (irreversible)
2. $CH_3^* + \frac{1}{2} H_2 \rightarrow CH_4 + ^*$ (irreversible)
3. $Cl^* + \frac{1}{2} H_2 \rightleftharpoons HCl + ^*$ (quasi-equilibrated)

Impact of the ACS-PRF Award on Students and the PI

This award has supported the research activities of two PhD students (Mohammed Al-Gharrawi and Jalal Tavana) and two undergraduates (Aiden Crane and Christopher Albert). Mohammed focused during the first part of the project on the construction and operation of a gas-phase mixed-flow reactor used to directly measure reaction rates, while Jalal has focused on the construction and operation of an *in situ* FTIR apparatus for observing the surface of working catalysts under reaction conditions. In the time since Mohammed left the research team, Jalal has assumed responsibility for both the reaction kinetics measurements and the *in situ* FTIR studies. Both graduate students attended the spring symposium of the New England Catalysis Society in 2018. Additionally, Jalal presented his preliminary data at the UMaine Student Symposium on Research and Creative Activity in 2018. All three students have learned to perform a variety of experimental techniques, including measuring reaction kinetics in both gas-phase and liquid-phase systems, gas chromatography and high-performance liquid chromatography, volumetric chemisorption measurements, and FTIR spectroscopy. Based on his undergraduate experience in the lab working on ACS-PRF-funded research, Christopher Albert has elected to pursue graduate studies and has joined the PI's lab as a new M.S. student working on a related project.

This award has had a significant impact on the PI, with funding from ACS PRF helping support a new research direction focused on C-X hydrogenolysis reactions in various systems. The ideas explored in this work, coupled with similar observations in other projects currently underway, will form basis for future proposals and a long-term research focus in C-X bond cleavage reactions. Moreover, the work from this project will result in several publications currently in preparation and has already facilitated the development of significant research infrastructure in our laboratory. The PI presented the results from this work at the Spring 2018 ACS Meeting in New Orleans, LA.

Preliminary Results

Reaction Kinetics Measurements:

The reaction kinetics of chlorobenzene hydrogenolysis have been measured over a low-dispersion Pd/C catalyst. This system shows no deactivation over 50 hours of time-on-stream, consistent with the observations of Aramendia and coworkers.⁵ Thus, catalyst deactivation in this system appears to be structure sensitive; on-going work in our lab will verify this conclusion.

The production rate of benzene over this catalyst shifts from first-order at 353 K to near-zero-order at 313 K. However, the reaction is half-order with respect to hydrogen over the same temperature range. Additionally, the reaction is inverse first-order with respect to HCl, and no kinetic isotope effect was observed in the presence of D₂. We constructed a microkinetic model of the reaction, using literature data to reduce the number of fitted parameters to 3. Figure 1 shows that the model captures the appropriate trends in the data; additional refinement of the fits is ongoing to achieve quantitative accuracy. The model assumes that C-Cl cleavage is rate-controlling, as expected based on Sequence 1. Moreover, only one site is required in the model, suggesting that hydrogenolysis occurs via insertion of a Pd atom into the C-Cl bond as suggested by Ribeiro and coworkers for chloroethane conversion.⁶

Kinetics measurements of the reaction over a Ni catalyst are ongoing. The reaction orders will be used to compare the mechanism against that observed for Pd, and the same microkinetic model will be used to evaluate this new data. Differences between Ni and Pd will be explained based on the microkinetics results.

Construction of in situ FTIR Cells:

Construction of a pair of *in situ* transmission FTIR cells and an accompanying volumetric dosing system was recently completed. One cell is designed for collecting spectra of probe molecules adsorbed on pre-treated catalyst samples. Coupled with a calibrated volumetric dosing system, this cell will be used for the measurement of molar extinction coefficients. The second cell is configured to observe working catalysts under reaction conditions. These cells will be used to evaluate the species abundant on the Pd catalyst surface under reaction conditions, and to measure enthalpies of adsorption of chloroaromatics on Pd surfaces (via van't Hoff analysis of isosteres).

References

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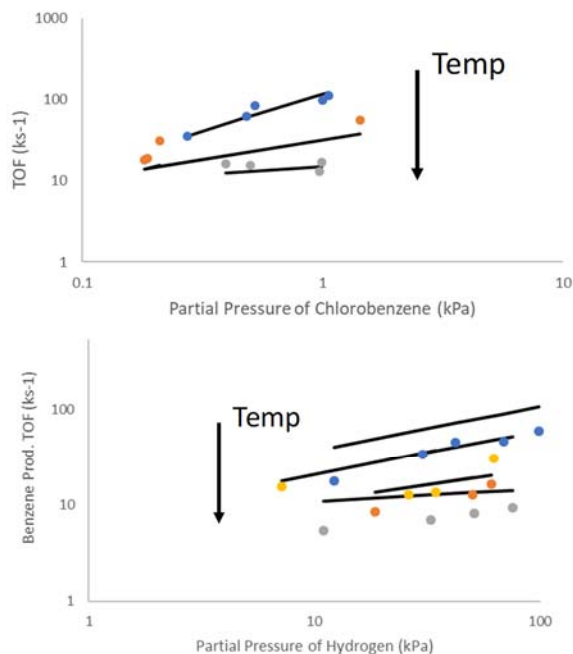


Figure 1. Influence of chlorobenzene and hydrogen partial pressures and temperature on the rate of benzene production. Solid lines show the fit of the microkinetic model. Temperature range from 353 K to 303 K. Rates were measured using 5% Pd/C at ~50% chlorobenzene conversion. He was used as a diluting gas where necessary. WHSV = 1-6 hr⁻¹.