SAND2022-9735D

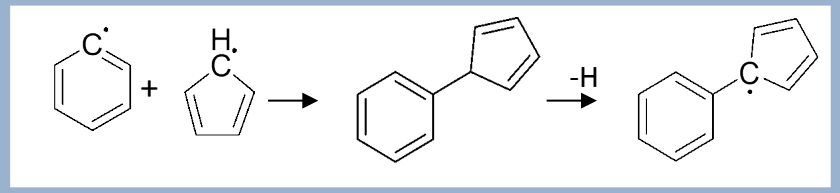
Sandia National Laboratories

Molecular weight growth by the phenyl + cyclopentadienyl reaction

Myrsini San Marchi (mmsanma@sandia.gov), *David E. Couch, Ahren W. Jasper, Goutham Kukkadapu, Angie J. Zhang, Craig A. Taatjes, Nils Hansen*
Gas Phase Chemical Physics Department, Sandia National Laboratories, Livermore, CA, USA

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are important precursors to soot formation. The goal of this experiment is to investigate radical-radical reactions as candidates for the formation of PAHs. Specifically, this experiment looks at the reaction between phenyl and cyclopentadienyl radicals. This reaction may be a good surrogate for reactions between larger 5- and 6-member ring radicals. These reactions create a loosely bound H atom, whose loss produces a larger radical.



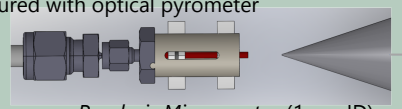
Phenyl (C_6H_5) Radical and Cyclopentadienyl (C_5H_5) Radical Reaction

Methods

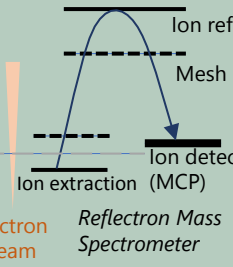
Experimental

Flows into silicon carbide pyrolysis microreactor where temperature is measured with optical pyrometer

Helium flows through parallel bubblers of nitrosobenzene (C_6H_5NO) and anisole ($C_6H_5OCH_3$)



Pyrolysis Microreactor (1mm ID) resistively heated to 800-1600K



Reflectron Mass Spectrometer

Simulation

Inputs:
- Initial Pressure
- Initial Mole Fraction
- Temperature Profile of Tube
- Initial Flow Rate
- Cantera File holding reaction rates

Matlab numerically solves the slip flow equations and chemical kinetic equations to simultaneously determine flow properties and chemical mole fractions at every point within the tube

Output: Mole Fraction of species exiting the tube

Results

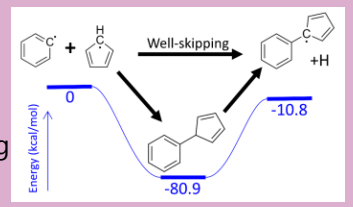
Precursors Break Down Into Radicals

Reactants produced in situ.

$$C_6H_5NO \rightarrow C_6H_5 + NO$$
$$C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3$$
$$C_6H_5O \rightarrow C_5H_5 + CO$$

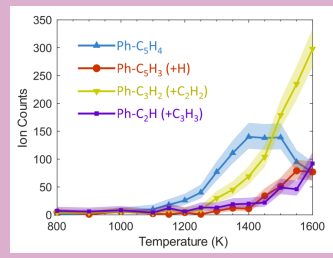
Radical Reaction

The cyclopentadienyl and the phenyl radicals react together to form C_6H_5-C_5H_5. This decomposes into the C_6H_5-C_5H_4 radical, in either a stabilization reaction or a well-skipping reaction.



Decomposition of Products

The C_6H_5-C_5H_4 radical is not very stable, so it will either continue to react and contribute to weight growth that will form larger PAHs, or it will decompose.



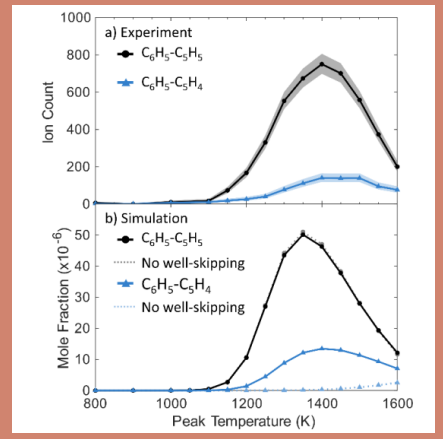
My Contribution

Simulation Comparison

- Updating the chemical kinetic mechanism in the simulation using more carefully calculated rates for important reactions

  $C_6H_5 + C_5H_5 <=> C_6H_5$-$C_5H_4 + H$

  $C_6H_5 + C_5H_5 <=> C_6H_5$-$C_5H_5$
- Running the simulation at each temperature that was studied experimentally
- Creating a figure comparing the simulation and the experiment



Trends of C_6H_5-C_5H_5 and C_6H_5-C_5H_4 are the same in the simulation and the experiment. When the well-skipping reaction was removed from the mechanism file, much less C_6H_5-C_5H_4 radical was formed which implies that the well skipping mechanism is significant.

Next Steps

Benzyne Chemistry

- Study the implications of the benzyne radical as an intermediate in soot formation
- React benzyne with other probable precursors to soot such as
  - Phenyl (C_6H_5)
  - Propargyl (C_3H_3)
  - Cyclopentadienyl (C_5H_5)
  - Benzyl (C_7H_7)
- Similar set up and simulations will be used

Conclusion

The radical reaction creates a PAH radical that had the potential to continue molecular weight growth to eventually form soot. Comparison between experiment and simulation reveals the role of well-skipping.

I acknowledge support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences. I also would like to thank Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.