Argonne NATIONAL LABORATORY

Chemistry Theory Overview

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Overview

Method Development

- Large Molecules

Applications

- Alcohols
- Biodiesel
- Foundational Chemistry

Accuracies

Method Development

Three Complexities for Large Molecules

- Accurate Energies
  - Size-Extensive Reduced Scaling MRSDCI
- Accurate Partition Functions
  - Multi-Structural Torsional Treatment
- Arbitrary Molecules
  - Reaction Mechanism Generator

Alcohols

$CH_3OH + HO_2, CH_3$

HO_2 + 1-butanol

C_4H_9O Decomposition

$C_4H_9O + O_2$

iso-butanol Decomposition

RMG mechanisms for all butanols

Esters

Thermochemistry

Methyl Formate for Validation

Abstractions by H, CH_3, O, OH, HO_2

Beta Scission

Calculations in progress for larger Esters

Foundational Fuel Chemistry

$H + HO_2$

$HCO + O_2$

$C_3H_6OOH + O_2$

Uncertainties

MRSDCI - Energies

Torsional Treatments

Ab Initio Rovibrational Analysis

Future

Better coupling between specific evaluations and development of general rules

Butanol

Abstraction by OH, HO_2, CH_3, for 1-butanol, isobutanol, and buteraldehyde

Decomposition of 1-butanol, 2-butanol, and t-butanol

Future

Esters

- Larger Esters
- Abstractions, Beta-Fission, Decomposition
- Kinetics

Foundational Fuels

- HO_2 + RO_2
- HO_2 + alkenols
- Butyl + O_2

Questions

Prioritization of our efforts is always needed.

How accurate do our rate coefficients need to be?

Should we be focussing our efforts on generating rate coefficients or on improving our methods?

What role do we want theory to play in C0-C4 mechanism developments?

Are we aiming for the mechanism or many individual mechanisms?

Are there needs for RMG that could benefit from the input of other theoreticians on the team?

Should we all be making group rules for RMG?

Do we want to make RMG a community tool?

Shouldn’t dimethyl ether really be one of our primary targets since this provides the best contact with the turbulence modeling.