Mechanism Thrusts Overview: Foundational Fuels, Butanols, and Esters (Biodiesel)

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Mechanisms: Status

- Foundational Fuels (C0-C4):
  - Very good new comprehensive validated model for H2/O2 (in press)
    - MUM-PCE of the underlying uncertainties (in planning)
  - Detailed study of propane ignition at low T (in preparation)
  - Some work on bigger species, building on JetSurf
    - Detailed study of low T propane ignition (in preparation)
    - Quantum thermochemistry for dozens of species
- Butanols:
  - Pretty good detailed comprehensive validated model for n-butanol.
    - Significant issues below 800 K.
    - Planning group publication.
  - Models for the other 3 isomers (2 published, 1 in preparation).
- Esters (Biodiesel):
  - Base kinetic model for methyl decanoate and butanoate developed.
    - Some improvement in ignition delay.
    - Large uncertainties in rate coefficients for H abstraction, radical isomerization, and decomposition of methyl ester molecules

Mechanisms: 'Minor' Technical Issues

- Several different simulators used in CEFRC, for different experiments.
  - Different assumed boundary conditions, handling of radiation, Soret effect, extrapolations, etc.
  - Some solvers have difficulty with large stiff mechanisms. Some of the stiff mechanisms are probably incorrect.
- Pressure dependent rate coefficients k(T,P)
  - Science issues: e.g. what is true $<\Delta E_{down}>$?
  - Representation issues:
    - Fit $k(T_n, P_n)$ accurately enough?
    - Monotonic interpolation, nothing crazy?
    - Solvers handle the representation?
- Validation data sets
  - Significant effort to gather data sets, get them into electronic form so they can easily be compared with computations.

Mechanisms: Big-Picture Issues

- Different goals lead to different mechanisms and different approaches to the mechanisms
- Clarity about the Goals is Key
- CEFRC focus: Primarily Methodology, not Individual Mechanisms
  - Develop Capability to Rapidly Assess Proposed Alternative Fuels
  - Good Mechanism-Building & Validation methods are useful for many fuels
  - Individual Mechanisms are Test Cases for Methods…
  - …but also reveal where improved understanding of chemistry (and chemistry-transport coupling) is needed. (Improved Understanding is also transferrable to many fuels).
  - Sensitivity analyses indicate that higher accuracy is needed in C0-C4 chemistry for all fuels: hence Foundational Fuels Thrust
- Improve integration of experiments and model-building
  - Experiment/Model/Experiment cycle time is pretty fast in the CEFRC, but still not perfectly smooth.

Goals for Foundational Fuels Thrust

- Very high accuracy individual numbers
- Methods for using/predicting experiments sensitive to multiple numbers
  - Can achieve higher accuracy in predictions by constraining the right combination of model parameters
  - Some individual numbers are not easy to determine accurately
  - Use our knowledge to design best “bang-for-the-buck” experiments.
- Careful assessment & use of uncertainties
- Hierarchical build-up of high-accuracy submodels

Foundational Fuels Challenges

- Some rate coefficients, thermo need to be known *very* precisely
  - Requires excellent experiments & calculations
- Most reactions have pressure effects; collider dependence
- Some key species and reactions are very difficult to probe experimentally
- Even though “small molecule”, still *many* species and reactions to consider.
- Many experiments sensitive to same set of rate coefficients, but hard to use all the data to constrain the rate coefficients:
  - Don’t have all the data, nor error bars on the data
  - Often not enough information to uniquely determine all the rate coefficients of interest.
  - Algorithms for extracting the information are not yet perfected.

Goals of Butanols Thrust

- Develop/Demonstrate Teamwork Approach to Mechanism Development
- Predictive Models for Many Alternative Fuels Desired – Butanols are a test case
  - How accurate are predictions?
  - How quickly can models be developed?
  - Which experiments are most helpful?
  - What are the pitfalls ?
- Improve understanding of alcohols chemistry.

Butanols Challenges

- *Lots* of species and reactions: order of magnitude greater than Foundational Fuels
  - Well-suited to automated model construction
  - Can build on Foundational Fuels submodels
- Very few rate coefficients known precisely; experiments typically constrain some combination of several model parameters.
  - Most numbers in models are estimates or quantum calculations.
- Multiple isomers, conformers, coupled rotors, isomerization reactions; lots of P dependence.

Goals of the Biodiesel Thrust

- Accurate understanding of the ester group chemistry for small methyl esters
  1. H abstraction reaction
  2. Radical decomposition and isomerization reactions
  3. Methyl ester decomposition reactions
- Effects of unsaturation
- Surrogate model for real biodiesel

Biodiesel Challenges

- Big molecules!
  - Many isomers, conformers, rotors
    - Many isomeric cyclic TS's and cyclic products
  - Many species and reaction steps are difficult to probe experimentally
    - Fast unimolecular reactions: too transient
    - Hard to distinguish isomers or to prepare specific isomers
    - Low volatility of some important species
    - Relatively few known rate coefficients or thermo
  - Computations are challenging
    - But we are developing quantum methods for big molecules
    - Need to upgrade solvers… or reduce kinetic models
- Ultimately we'd like a surrogate for B10
  - Challenges of diesel surrogate combined with challenges of pure biodiesel surrogate

Mechanism Thrusts Differ, But Are Strongly Coupled

- All models depend on Foundational Fuels submodels, rate coefficients, thermo.
- How precise do Foundational Fuels submodels have to be achieve desired accuracy in Butanol and Biodiesel models?
- Rate estimation techniques from Butanol study useful for Biodiesel models.
- Automated model construction should help with Biodiesel… but computer methods need improvements to effectively handle vast number of species and reactions.

Next Steps for Mechanism Thrusts

This afternoon, CEFRC breakout groups will focus on planning next steps.

+ Arranging collaborations

+ Debating proposed plans

Tomorrow morning we'll present a summary of our plans, both short-term and long-term.

Schedule of Discussions

- 1:00 – 1:30 Solvers, Experimental Database representations including Uncertainties, k(T,P) representations
- 1:30 – 2:00 Fundamental Fuels (C0-C4)
  - Including DME
- 2:00 – 2:30 Butanol
- 2:30 – 3:00 Esters (Biodiesel)

We don't expect everyone to attend all four after lunch discussions.

Perhaps we should discuss how the team can work more effectively with RMG sometime after the 3:00 break?