Impact of Fuel Structure on Ignition Kinetics

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Objective:

- Develop improved models to assess impact of alternative fuels on Navy combustors
- Develop theoretically based rate estimation rules for incorporation into LLNL fuel oxidation mechanisms
- Predict impact of volatility differences of fuels on combustion events
- Deliver mechanisms and mixing models to UTRC for predictions in real combustors

Approach:

- Use high-level electronic structure calculations on small alkane systems to obtain detailed understanding of low-T oxidation chemistry
- Generalize validated individual rate expressions to create rate estimation rules applicable for larger hydrocarbons
- Collaborate with LLNL to incorporate rate rules into their mechanisms
- Develop two-phase flow models to account for impact of vaporization rate on combustion
- Validate models with USNA data

Scientific or Naval Impact/Results:

- Developed rate rules for RO₂ reactions and delivered to LLNL
- Demonstrated that high-pressure rate rules suitable for ignition calculations
- Developing rate rules for QOOH reactions
- Developed multicomponent vaporization model and calculated impact of drop size, temperature, pressure, fluid-mechanical strain, droplet composition, droplet size, and droplet loading density
Goal: Develop Rate Rules for Diesel Ignition

Rules needed for $RO_2$, $Q^\ddagger$OOH, and $HOOQOO^\ddagger$ reactions
Both rate constants and thermo important
Path from Electronic Structure Calculations to Pressure-Dependent Rate Constants

- **Gaussian Software®**
  - Geometry, Frequencies, Electronic Energy, Dipole Moment, Polarizability, ...
- **FANCY**
  - Heat of Formation, Entropy, Heat Capacity
  - 3-Freq Representation, NASA Polynomials
- **TSTdG**
  - High-pressure Rate Constants $k_\infty(T)$ for Elementary Reactions
- **CHEMDIS**
  - Pressure-dependent Rate Constants $k(T,P)$ for Chemically-activated Reactions
Fast Isomerization of CCOO⁻ Adduct Leads to Chain Branching

- Only important pathways for n-propyl + O₂ are isomerization, concerted elimination and redissociation
Slower Isomerization of CC(OO$^\cdot$)C Adduct Leads to Chain Inhibition

- **Concerted elimination dominant** for isopropyl + O$_2$
  - branching pathway inhibited
- Detailed calculations show other pathways can be neglected
Unadjusted Ab-initio Predictions Quantitatively Describe Propane Oxidation

However, reaction pathways in CSM model much different from Galway mechanism (that uses LNLL rate rules)


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Significantly Different Pathways in CSM vs. Galway Models

Primary Pathways in CSM Model

CCC• dominates ignition kinetics since CC(OO•)C isomerization rate slow relative to concerted elimination of HO₂

Primary Pathways in Galway Model

Both CCC• and CC•C important since CC(OO•)C isomerization much faster in this mechanism
Extension to Larger Hydrocarbons

• Despite complexity of underlying potential energy surfaces, only a few reaction pathways are important.

• Approach to develop rate rules applicable to larger systems:
  ➢ Use high-level theory for C2-C6 hydrocarbons
  ➢ Generalize results on a per-site basis and use these for larger species
  ➢ Use rule based rate constants as input for pressure-dependence analysis for recombination and addition reactions

• Transfer rate rules to LLNL for incorporation into their mechanisms
Calculated Rate Constants for a Given C-H Type Are Constant for H Abstraction From Alkanes By H Atoms
Important $R + O_2$ Reaction Channels

- $RO_2$ dissociation
- $RO_2$ isomerization
- $RO_2$ concerted elimination
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- Depends on ring size and overall thermochemistry.
- Significantly different from hydrocarbon analogs.
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Isomerization Reaction Subsets Group Nicely

- Calculations allow quantification of Benson’s ideas
  - Barrier depends on ring strain and enthalpy change
  - A-factor strongly affected by loss of rotors in TS
Unlike other reactions, very little effect of structure.
One rate constant seems sufficient for linear and branched alkyl peroxy radicals.
Competition between dissociation and isomerization for $\text{RO}_2$

- 6- and 7-member transition state isomerizations much faster than 5-member
Isomerization Dominates RO₂ Reactions

- Numerical integration results at 750K with n-C₈ as reactant
- Results verify that high-pressure values are adequate
- γ-QOOH product reflects faster rate for 6-member TS
- 7-member TS product next most important
Important Q‧OOH and HOOQOO‧ Reactions

- Q‧OOH cyclic ether formation
- Q‧OOH isomerizations
- 2\textsuperscript{nd} $O_2$ addition

- HOOQOO‧ isomerizations
- HOOQOO‧ cyclic ether formation
- HOOQOO‧ dissociation (in progress)
$RO_2 = Q\cdot OOH$ Equilibrium Sensitive to Structure

- Equilibrium shifted strongly toward more stable reactants
- Expect much higher concentration of tertiary QOOH
Oxirane Formation Surprisingly Fast

A-factors behave as expected in terms of restricted rotors, but very low barrier for 3-member ring
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QOOH Competitive Reactions Sensitive to Structure

- Very complex interplay among various channels
- Second O₂ addition scales linearly with pressure
- Difficult to generalize without extensive kinetic calculations
Inclusion of QOOH Reactions Dramatically Shifts Product Slate

- Reverse reaction of QOOH to RO₂ critical to product evolution
Methyl Branch Inhibits Ignition

- OH/OH\(_2\) much greater for n-butane
- Consistent with faster ignition

HO$_2$ Production Rate Similar for Both Structures

- Formed from the concerted elimination of the alkyl peroxy radical
More Impact of Structure for OH Production

For iso-butane, OH is primarily produced though QOOH cyclic ether pathway.

For n-butane, OH is primarily produced though $O_2QOOH$ 1-5 isomerization.
Summary/Plans

• CBS-QB3 results successfully predict propane ignition
  – Suggest significantly different reaction pathways
• Subsequent calculations confirm similarity of reaction rate constants
  – Possible to generalize results to extract rate rules
• Rules generated for R+O₂ and Q*OOH reactions
  – Include both rate constants and thermo
  – Results suggest substantial impact of structure
    – High-pressure values should be adequate for most systems of interest

• Now working on ¢OOQOOH reactions

• Multicomponent vaporization analysis being extended to consider (reduced) detailed gas-phase reactions for counterflow diffusion flames
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