Combustion Studies of Alcohols, Esters and Hydrogen Rich Fuels

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Overview

Fuels Combustion Research Laboratory’s contribution to CEFRC efforts

- Generation of motivating fundamental experimental observations that elucidate the interactions of bio-derived molecular components and structures with components found in petroleum derived fuels.
- Provision of experimental validation data for development and refinement of detailed kinetic models for esters and alcohols.
- Experimental determination of elementary kinetic rates important to the decomposition and oxidation of hydrocarbons and hydrocarbon oxygenates.

Accomplishments

- Chemical Kinetics of iso-Propanol and t-Butanol Pyrolysis and Oxidation
- Auto Ignition of n-heptane/Butanol Blends in Ignition Quality Tester
- Methyl Formate Decomposition, and Oxidation in Low Pressure Flames
- An Updated Kinetic/Transport Model for H$_2$/O$_2$ Sub-model improvements
Chemical Kinetics of *iso*-Propanol and *t*-Butanol Pyrolysis and Oxidation

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“Next-generation” biofuels – Alcohols

Flow reactor study on iso-propanol and tert-butanol

Motivation

- Lower soot / polyaromatic hydrocarbon emissions.
- Few studies on next generation, higher molecular weight oxygenated fuels → Experimental data needed for extensive model validation.
- Experimental determination of the dehydration rate constants for n/i-propanol and tert-butanol.
- Detailed speciation data for alcohol oxidation obtained at T<950 K.
- Detailed mechanistic study is needed to understand the combustion of these alcohols and interactions with two stage kinetics of large carbon number hydrocarbons.
## Experimental conditions

### Iso-propanol

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T (K)</th>
<th>P (atm)</th>
<th>Molar conc’n (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis History</td>
<td>800 – 1000</td>
<td>12.5</td>
<td>5000</td>
</tr>
<tr>
<td>Pyrolysis Reactivity (τ = 1.8 s)</td>
<td>550 – 1025</td>
<td>12.5</td>
<td>5000</td>
</tr>
<tr>
<td>Oxidation Reactivity (τ = 1.8 s, φ=1)</td>
<td>520 – 1010</td>
<td>12.5</td>
<td>2500</td>
</tr>
<tr>
<td>Pyrolysis with radical trapper (1,3,5-TMB)</td>
<td>900 – 1000</td>
<td>12.5</td>
<td>1200 equimolar</td>
</tr>
</tbody>
</table>

### Tert-butanol

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T (K)</th>
<th>P (atm)</th>
<th>Molar conc’n (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis History</td>
<td>720–1000</td>
<td>12.5</td>
<td>2500</td>
</tr>
<tr>
<td>Pyrolysis Reactivity (τ = 1.8 s)</td>
<td>500 – 975</td>
<td>12.5</td>
<td>2500</td>
</tr>
<tr>
<td>Oxidation Reactivity (τ = 1.8 s, φ=1)</td>
<td>676 – 918</td>
<td>12.5</td>
<td>2500</td>
</tr>
<tr>
<td>Pyrolysis with radical trapper (1,3,5-TMB)</td>
<td>1020, 1080</td>
<td>3.0</td>
<td>1540 equimolar</td>
</tr>
</tbody>
</table>
Preliminary results on pyrolysis/oxidation

- Level to which water and olefin yield in equal quantities gives evidence of radical trapper methodology. Rate of dehydration reaction extracted experimentally
  
  \[
  \begin{align*}
  \text{iso-propanol:} & \quad i-C_3H_7OH \leftrightarrow C_3H_6 + H_2O \\
  \text{tert-butanol:} & \quad t-C_4H_9OH \leftrightarrow C_4H_8 + H_2O 
  \end{align*}
  \]

- Radical trapper addition to extract water elimination rate constant

- Oxidation reactivity profiles (no reactivity at T < 775K)

\[ \text{iso-propanol pyrolysis with radical trapper:} \]

- 1200 ppm \( i-C_3H_7OH \)
- 1200 ppm 1,3,5-TMB
- \( P = 12.5 \) atm

\[ \text{Oxidative conditions:} \]

- \( P = 12.5 \) atm
Autoignition of Fuel/Butanol Blends in an Ignition Quality Tester

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Princeton University
Autoignition of Butanol?

Motivation

- Isomers of butanol have been identified as promising candidates of 2nd generation bio fuels.
- Little fundamental work available on how these alcohols interact with hydrocarbons found in conventional petroleum derived fuels—likely end use scenario for these bio generated materials.

Objectives

- Scan ignition behavior trends in isomeric structures.
  - Engine-relevant pressure, temperature and fuel loading.
  - Identify “interesting” behaviors to focus more fundamental studies.
- Examine kinetic coupling of components in fuel blends.

Experiments: A study of comparative ignition quality

- Trends in reactivity extendable to conventional HCSI, DI engine applications as well as high-efficiency PCCI future designs.
- Comparisons among butanols at similar volumetric blending in n-heptane and a real low-cetane diesel fuel.
Reactivity Trends – Neat Butanols

<table>
<thead>
<tr>
<th>Pure Component</th>
<th>Avg. Measured DCN</th>
<th>MON</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-butanol</td>
<td>&lt;7.18</td>
<td>94</td>
</tr>
<tr>
<td>i-butanol</td>
<td>8.51</td>
<td>94</td>
</tr>
<tr>
<td>2-butanol</td>
<td>8.54</td>
<td>91</td>
</tr>
<tr>
<td>n-butanol</td>
<td>12.02</td>
<td>78</td>
</tr>
<tr>
<td>n-heptane</td>
<td>53.8†</td>
<td>0†</td>
</tr>
</tbody>
</table>

Increasing Reactivity

1-butanol  (+/−)2-butanol  i-butanol  t-butanol (TBA)

α-hydrogen C–H bond sites indicated
Reactivity Trends – Blends

Increasing alcohol content

t-butanol shows significantly different behavior

Blended with diesel fuel (solid lines)

DCN sensitivity of -0.33 DCN/vol% Blended with n-heptane
Proposed Mechanism for TBA Behaviour

Radical pool generation relatively slow in pure TBA

- Unimolecular processes slow at IQT conditions, mostly abstraction reactions governing ignition.
- Low temperature O₂ addition reactions evidently less important (Cullis & Warwicker) than for large carbon number hydrocarbons.
- β hydrogen atoms less prone to abstraction than α atoms
  BDEs of ~101 vs. 93–95 kcal/mol.
- Subsequent radical decomposition leads to straight-chain reactions and stable products.

\[ X + \text{TBA} \rightarrow XH + \cdot \text{CH}_2(\text{C})(\text{CH}_3)_2\text{OH} \]  
\[ \cdot \text{CH}_2(\text{C})(\text{CH}_3)_2\text{OH} \rightarrow \text{i-butene} + \text{OH} \]  
(β-scission)

for X=OH, product is H₂O

Key difference between TBA & other BuOHs is selectivity of OH generation process: other BuOHs will mostly produce less reactive HO₂ radical.
Methyl Formate Decomposition, and Oxidation in Low Pressure Flames

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Motivation – (1) Diesel Combustion

- Methyl formate (MF) is major intermediate in Dimethoxy methane (DMM) oxidation and dimethyl ether (DME) oxidation in presence of NO\textsubscript{x}.
- Understanding chemical mechanism of MF oxidation $\Rightarrow$ refine understanding of DMM/DME oxidation.

Motivation – (2) Biodiesel Combustion

- Biodiesel consists primarily of long alkyl chain methyl esters.
- Role of ester functionality on biodiesel oxidation remains to be fully understood quantitatively.
- Study of smaller carbon number esters can lead to better understanding of functional behavior in large carbon number species.

Methyl formate is simplest methyl ester.
Methyl Formate Kinetic Model

- Validation – High temperature shock tube ignition delays.
  - Laminar burning velocities.

MF shock tube ignition delay times. Experiment (symbols) and simulation (lines).

Laminar burning velocities of MF/O₂/N₂ freely propagating flames at 1 atm. Experiment (symbols) and simulation (line).
Flow reactor speciation data measure methanol, formaldehyde and methane from MF oxidation.

Pyrolysis measurements show large amounts of methanol and carbon monoxide, indicative of molecular decomposition of methyl formate.

Kinetics of MF decomposition highly contentious, reported activation energies span 48-77 kcal mol^{-1}(!)

Speciation data from flow reactor oxidation of 0.005/0.01/0.985 MF/O_2/Ar, φ=1.0, at 3.0 atm and 975K (top) and 900 K (bottom). Experiment (symbols) and simulation (lines). Rate constant data for MF decomposition.
Methyl Formate Decomposition

Potential effect of wall catalytic reactions evaluated by conducting LES of the entire VPFR geometry.

\[
\text{CH}_3\text{OCHO}_{(\text{surface})} \leftrightarrow \text{CH}_3\text{OH}^*_{(\text{surface})} + \text{CO}^*_{(\text{surface})}
\]

Products of wall catalytic processes confined in the viscous sub-layer region.

Heterogeneous surface perturbations cannot significantly affect the measurement of the gas phase reaction (of negligible quantity at the center line less than 4%)

Calculated concentration of CH3OH* in the reactor environment at 975 K, 3 atm, 14.344 g/s flow rate of 5000 ppm of MF in N₂.

Axial profile of MF and gas phase (methanol) vs potential heterogeneous catalytic (methanol*) products for 5000 ppm MF in N₂ at 3 atm at the center line (lines and symbols represent calculations and experiments, CO omitted for clarity)
Experimental data (symbols) and simulation (lines) of MF oxidation in MF/O₂/Ar, Φ = 1.0–1.8, 22–30 Torr flames

- Model captures experimental measurements well.
- Manuscript in review with further details and analyses.
Updated $\text{H}_2/\text{O}_2$ Kinetic Transport Model to Address High Pressure Flame Modeling difficulties

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$^2$F. M. Global
$^3$Argonne National Laboratory
Motivation

- H₂/O₂ kinetic sub-model – Fundamental topic w/ applications:
  - Hierarchical development of all HC kinetic models.
  - Accurate kinetic/transport models needed for syngas and high hydrogen content fuels to be used in IGCC applications.
- High pressure, low flame temperature, fuel-lean and/or diluted combustion conditions used in most applications (to control NOₓ emissions).

Substantial H₂/O₂ modeling difficulties in high-pressure dilute flames

H₂/O₂ modeling difficulties affect high-pressure HC flame predictions


Updated H₂/O₂ Kinetic–Transport Model

- Updated model uses the 19–reaction mechanism of Li et al.
  - To incorporate recent studies on elementary reactions.
  - To improve model performance at high–pressure flame conditions.
- Treatment of the following processes/reactions were revised:
  - Temperature and pressure dependence of HO₂ formation / consumption reactions:
    - H+O₂(+M)=HO₂(+M)
    - HO₂ + H/O/OH/HO₂
  - Other reactions updated:
    - e.g. H₂O₂(+M)=OH+OH(+M), OH+H₂O₂=H₂O+HO₂, H+OH+M=H₂O+M.
  - Transport updated:
    - e.g. H, H₂.
- Major sources of remaining uncertainties:
  - Temperature (and pressure) dependence of HO₂+H/OH/O/HO₂.
  - Fall–off behavior and mixture rules for H+O₂(+M)=HO₂(+M).

Nonlinear Bath–Gas Mixture Interaction

- Practical combustion => multi-species bath gas.
- At best, models assume linear mixture rule:
  \[ k = \sum k_i(T, P) \cdot X_i \]
  At worst, common modeling approaches yield \( n \) times high-pressure limit => but
- Different components of a multi-component bath gas “interact” in unimolecular reactions
- Nonlinearities stronger when:
  - \(<\Delta E>\) difference is larger
  - Each component has nearly equal contributions to rate constant
  - Reaction is in intermediate fall-off
- Preliminary calculations and those of Troe (1980) show ~10% nonlinearities in low-p limit
- ~10% mixing effects yield 15% differences in burning rate predictions
- Behavior highly dependent on \(<\Delta E>\) values


Updated Model Performance

- Reproduces previous validation targets of Mueller et al. and Li et al. including flow reactor speciation, ignition delays, and flame speeds.

- Shows significant improvements against high-pressure, low-flame-temperature data.

- Predicts wide range of flame speed targets within 20%.

Future Plans

- Continuing efforts to contribute elementary rate constant measurements and kinetic system validation data using flow reactor techniques.

- Contributions to the small molecule chemistry that is important to high pressure oxidation kinetics of these materials.

- Development of chemical kinetics model for bio-derived fuels.
Acknowledgments

- **Research Staff:** Drs. Stephen Dooley, Saeed Jahangirian, and Tanvir Farouk
- **Graduate Students:** Francis M. Haas, Joshua S. Heyne, Michael P. Burke, Zeynep Serinyel
- **Undergraduates:** Amanda Ramcharan
- **Technical Staff:** Timothy Bennett, John Grieb, Joseph Sivo
- **Collaborations**
  - Dr. Steven Klippenstein (Argonne National Laboratory)
  - Drs. Nils Hansen and Bin Yang (Sandia National Laboratories)
  - Dr. Terrance Cool (Cornell University)
  - Dr. Henry Curran (National University of Ireland, Galway)