Flame Chemistry and Diagnostics

High-Temperature Oxidation of (1) \( n \)-Butanol and (2) \( C_4 \)-Hydrocarbons in Low-Pressure Premixed Flames

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Outline

- Background and Motivation
- Experimental Details
  - Photoionization Mass Spectrometry
  - Targeted Flame Conditions
- n-Butanol Flame Chemistry
- C₄- Hydrocarbons Flame Chemistry: *iso*-butene as a test case
Background and Motivation

✓ *n*-Butanol

- Several studies have been targeted on a fundamental understanding of its combustion chemistry
- Models are best tested against *in-situ* species measurements in simple (laminar, premixed) burner-stabilized flames. Detailed species profiles will provide a very strict test of the combustion chemistry models.

✓ *C*₄- Hydrocarbons

- *C*₄-hydrocarbons combustion data are still of scarcity except for 1,3-butadiene. Combustions of 1-butene (1-C₄H₈), *n*-butane (C₄H₁₀), *iso*-butene (iC₄H₈), *iso*-butane (iC₄H₁₀) at both fuel-rich and stoichiometry conditions are desired
- In particular, *iso*-butene is an important intermediate of the pyrolysis and oxidation of *iso*-butanol.
Flames are analyzed with molecular beam time-of-flight mass spectrometry.

Photoionization with tunable synchrotron-generated VUV photons allows identification of species:
- by mass
- by ionization energy

Experimental mole fraction profiles are compared with flame model predictions.

Reaction path and sensitivity analysis are performed.
## Experimental Details

### Targeted \( n-C_4H_9OH \) Flame Conditions

<table>
<thead>
<tr>
<th></th>
<th>Flame 1</th>
<th>Flame 2</th>
<th>Flame 3</th>
<th>Flame Oßwald*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n-C_4H_9OH )</td>
<td>3.6</td>
<td>3.3</td>
<td>7.2</td>
<td>17.8</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>24.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O_2 )</td>
<td>24.1</td>
<td>16.7</td>
<td>42.8</td>
<td>57.2</td>
</tr>
<tr>
<td>( Ar )</td>
<td>48.2</td>
<td>80.0</td>
<td>50.0</td>
<td>25</td>
</tr>
<tr>
<td>pressure</td>
<td>15</td>
<td>25</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Equivalence Ratio</td>
<td>1.4</td>
<td>1.2</td>
<td>1.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>


More than 40 isomer-resolved species with ion masses ranging from 2 (\( H_2 \)) to 74 (\( C_4H_9OH \)) are quantified for each flame.
## Targeted C₄- Flame Conditions

<table>
<thead>
<tr>
<th></th>
<th>iC₄H₈</th>
<th>iC₄H₈</th>
<th>iC₄H₁₀</th>
<th>iC₄H₁₀</th>
<th>1-C₄H₈</th>
<th>1-C₄H₈</th>
<th>C₄H₁₀</th>
<th>C₄H₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalence Ratio</td>
<td>1.60</td>
<td>1.00</td>
<td>1.60</td>
<td>1.00</td>
<td>1.60</td>
<td>1.00</td>
<td>1.60</td>
<td>1.00</td>
</tr>
<tr>
<td>C/O ratio</td>
<td>0.53</td>
<td>0.33</td>
<td>0.49</td>
<td>0.31</td>
<td>0.53</td>
<td>0.33</td>
<td>0.49</td>
<td>0.31</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Inlet velocity (cm/s)</td>
<td>44.8</td>
<td>67.2</td>
<td>44.8</td>
<td>67.2</td>
<td>44.8</td>
<td>67.2</td>
<td>44.8</td>
<td>67.2</td>
</tr>
<tr>
<td>Fuel (slm)</td>
<td>0.316</td>
<td>0.214</td>
<td>0.296</td>
<td>0.200</td>
<td>0.316</td>
<td>0.214</td>
<td>0.296</td>
<td>0.200</td>
</tr>
<tr>
<td>O₂ (slm)</td>
<td>1.184</td>
<td>1.286</td>
<td>1.204</td>
<td>1.300</td>
<td>1.184</td>
<td>1.286</td>
<td>1.204</td>
<td>1.300</td>
</tr>
<tr>
<td>Ar (slm)</td>
<td>1.500</td>
<td>1.500</td>
<td>1.500</td>
<td>1.500</td>
<td>1.500</td>
<td>1.500</td>
<td>1.500</td>
<td>1.500</td>
</tr>
</tbody>
</table>

![Chemical structures](image-url)
The n-butanol mechanism has been generated with the RMG of the Green group.

Simulations of the low-pressure flames are sensitive to the \( i-C_{4}H_{5} (CH_{2}=CH-\bullet C=CH_{2} \leftrightarrow \bullet CH_{2}-CH=C=CH_{2}) \) thermochemistry, but are not for the shock tube, RCM, and JSR experiments.
Mole fraction profiles of the major species are predicted accurately.

A more powerful test is provided by comparing modeled and experimental profiles of intermediate species.
**n-Butanol:** Flame Chemistry Insights

Conceivable *n*-Butanol Consumption Pathways

\[
\text{CH}_3 + \bullet \text{HOH} \rightarrow \text{CH}_3 + \text{HOH}
\]

\[
\text{C}_4\text{H}_9\text{O} \rightarrow \alpha\text{-C}_4\text{H}_9\text{O}
\]

\[
\beta\text{-C}_4\text{H}_9\text{O} \rightarrow \gamma\text{-C}_4\text{H}_9\text{O} \rightarrow \delta\text{-C}_4\text{H}_9\text{O}
\]

\[
\text{C}_4\text{H}_8\text{Oenol} \rightarrow \text{C}_4\text{H}_8\text{Oenol2} \rightarrow \text{C}_4\text{H}_8\text{Oenol3}
\]

\[
\text{CH}_2\text{O} \rightarrow \text{CHOH} \rightarrow \text{C}_4\text{H}_8\text{Oenol} \rightarrow \text{C}_4\text{H}_8\text{Oenol2} \rightarrow \text{C}_4\text{H}_8\text{Oenol3}
\]

\[
\text{CH}_3 + \text{HOH} \rightarrow \text{CH}_3 + \text{HOH}
\]
The formation of the CH₃CH₂CH₂CH₂CHOH (α-C₄H₉O) radical is predicted to be slightly preferred.

The fission of C-C bonds of n-butanol are only significant at high temperatures of the Oßwald et al. flame.
Flame Chemistry Insights
Consumption of the $\alpha$-$\text{C}_4\text{H}_9\text{O}$ Radical

$\text{CH}_3$-$\text{CH}_2$-$\text{CH}_2$-$\bullet$-$\text{CH}$-$\text{OH}$

- $n$-$\text{C}_4\text{H}_9\text{OH} + O = \alpha$-$\text{C}_4\text{H}_9\text{O} + \text{OH}$
- $n$-$\text{C}_4\text{H}_9\text{OH} + \text{H} = \alpha$-$\text{C}_4\text{H}_9\text{O} + \text{H}_2$
- $n$-$\text{C}_4\text{H}_9\text{OH} + \text{OH} = \alpha$-$\text{C}_4\text{H}_9\text{O} + \text{H}_2\text{O}$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{O}_2 = n$-$\text{C}_4\text{H}_9\text{O} + \text{HO}_2$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{O}_2 = \text{C}_4\text{H}_8\text{Oenol} + \text{HO}_2$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{O}_2(+\text{M}) = \text{C}_4\text{H}_8\text{Oenol} + \text{HO}_2(+\text{M})$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{H} = \text{C}_3\text{H}_7 + \text{CH}_2\text{OH}$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{H} = \text{C}_2\text{H}_5 + \text{CH}_2\text{CH}_2\text{OH}$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{H} = \text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- $\alpha$-$\text{C}_4\text{H}_9\text{O} = \text{C}_2\text{H}_5 + \text{CH}_2\text{CHOH}$

- The $\alpha$-$\text{C}_4\text{H}_9\text{O} + \text{O}_2$ reaction is the main route to $n$-butanal
- Oßwald et al. did not separate butenols from $n$-butanal
**n-Butanol:**

**Flame Chemistry Insights**

**Consumption of the β-C₄H₉O Radical**

\[ \text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_2\text{-OH} \]

- The decomposition of β-C₄H₉O is the main route to 1-butene
- Formation of a propenol isomer is not significant
Summary

- Three sets of low-pressure \( n \)-butanol flames have been measured
- The model's predictive capabilities for high-temperature oxidation of \( n \)-butanol have been improved
- \( n \)-butanol oxidation is initiated by H-abstraction by H, O, and OH – formation of \( \alpha \)-C\(_4\)H\(_9\)O is preferred
- C-C bond fissions are only important at high temperatures and the water-elimination reaction is not important under the current conditions
- Subsequent disproportionation reactions of the C\(_4\)H\(_9\)O radicals and fast \( \beta \)-scissions govern the formation of smaller intermediates
- A paper describing the model has been submitted to *Phys. Chem. Chem. Phys.*

Outlook

- Experimental (and modeling) work of flames fueled by *iso*-butanol are (almost) completed and will be presented next year
- We initiated work on *iso*-pentanol
Major Species in *iso*-Butene Flame

- USC Mech II and imposed, experimental temperature
- Discrepancies very near the burner: Uncertainties in local temperature and sampling-cone effect
C₄- Flames:

Minor Species for Fuel-rich *iso*-Butene Flame

- Well predicted profiles for most flame intermediates
- C₄H₄ and C₄H₆ are underpredicted
- The USC model requires further improvement for low-pressure isobutene flames
C₄- Flames:

Rates of Production and Consumption

**iso-Butene**

\[ \text{ROP GasRxn_Total (mole/cm}^3\text{sec)} \]

Distance from Burner (mm)

\[ i\text{C}_4\text{H}_8 \rightarrow i\text{C}_4\text{H}_7 \rightarrow \text{aC}_3\text{H}_4 \]

\[ \text{CH}_3\text{CCH}_2 \]

**iC₄H₇**

\[ \text{ROP GasRxn_Total (mole/cm}^3\text{sec)} \]

Distance from Burner (mm)

\[ i\text{C}_4\text{H}_8+\text{OH}=i\text{C}_4\text{H}_7+\text{H}_2\text{O} \]

\[ i\text{C}_4\text{H}_7+\text{H}=\text{CH}_3\text{CCH}_2+\text{CH}_3 \]

\[ \text{Total} \]

\[ a\text{C}_3\text{H}_4+\text{CH}_3=i\text{C}_4\text{H}_7 \]

\[ i\text{C}_4\text{H}_7+(+\text{M})=i\text{C}_4\text{H}_8(+\text{M}) \]
Rates of Production and Consumption

**C₄- Flames:**

**CH₃CCH₂ Radical**

**Benzene**

- More benzene formation than the normal alkene
- $i\text{C}_4\text{H}_7 \rightarrow C_4$ species?
**C₄- Flames:**

**Missing Reactions for C₄ - Species**

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{CH}_2 \quad + \ M \quad \rightarrow \quad \text{H}_3\text{C} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad + \ M \quad - \ H \quad \rightarrow \quad \text{H}_2\text{C} \quad = \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad = \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad + \ H \ (-H) \quad \rightarrow \quad 1,3\text{-C}_4\text{H}_6 \\
\text{H}_2\text{C} \quad = \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad + \ M \quad \rightarrow \quad 1,3\text{-C}_4\text{H}_6
\end{align*}
\]
Predicts reasonably well the shape and magnitude of the newer flame speed curve.
**C₄- Flames:**

**Ignition Delay Time**

- The predicted ignition delay times are higher than the experimental data at lower temperatures (1300-1500K)
- Missing C₄- reactions and uncertainty for reaction rate constants of fuel decomposition

C₄- Flames:

Complementary Laser-Based Set-up

- Laser-induced fluorescence (LIF)
- Resonantly enhanced multi-photon ionization (REMPI)
  - mass selected detection of PAHs
  - large dynamic range – PAH concentrations vary (~1000 ppm – 100 ppb)
C₄- Flames: REMPI

- Phi=1.6 flames
- 263 nm; 225mj; 4000 shots
- Iso-isomers have larger soot-tendency
Flame species profiles have been measured by MBMS

Missing pathways: $iC_4H_7$ to 1,3-butadiene

Revisions and updates are required for the reaction chemistry of isobutene pyrolysis and oxidation to improve the model’s predictive capabilities

Quantitative mole fraction profiles for REMPI-MBMS measurements

Updated $C_4$- hydrocarbons kinetics model