High-Temperature Oxidation of \( n \)-Butanol, \( iso \)-Butane, and \( iso \)-Butene in Low-Pressure Premixed Flames

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✓ **Experimental Details**
  - Photoionization Mass Spectrometer
  - Flame Conditions

✓ **Flame Chemistry Insights (n-butanol flame)**
  - Experiment vs. Model
  - Fuel-Consumption Pathways
  - Enols and Aldehydes: Reaction Path Analysis

✓ **Summary and Outlook**
Experimental Details: Synchrotron Photoionization Molecular-Beam Mass Spectrometry

- Premixed laminar low-pressure flames
- Molecular beam sampling "freezes" chemistry
- Time-of-flight mass spectrometry offers the appeal of universal and relatively rapid data collection
- Photoionization mass spectrometry allows identification of species
  - by mass
  - by ionization energy
- Energy Scan:
  - to identify species by photoionization efficiency curves
- Burner Scan:
  - to get spatial profiles the burner is moved relative to the quartz cone and photon energy is fixed
Experimental Details: Synchrotron Photoionization Molecular Beam Mass Spectrometry

- **Burner Scan**
  to get spatial profiles the burner is moved relative to the quartz cone and photon energy is fixed

- **Energy Scan**
  to identify species by photoionization efficiency curves the photon energy is scanned and the burner position is fixed

![Graphs and images showing experimental results for Ethene flame $\Phi = 1.9$ and other measurements.](image-url)
about 30 to 40 species were quantified for each flame

- temperature profiles were measured using OH LIF
- resulting mole fraction data are compared with combustion chemistry model predictions

### Experimental Details: Flame Conditions and Combustion Chemistry Models

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n-butanol: Experiment vs. Modeling (Harper et al.)

- The updated model includes additional pressure-dependent rate coefficients
  - *the model was insensitive to these kinetic parameters for the previous validation targets*
- experimentally determined major species profiles agree satisfactorily with modeled results
- larger discrepancies for some minor species, including C₃’s and C₄’s
**n-butanol: Fuel-Consumption by H-Abstraction Reactions**

**First Steps in Fuel-Consumption:**
- Fuel-consumption is initiated by H-abstraction reaction with H, O, and OH and formation of the isomeric $C_4H_9O$ radicals
- $C_4H_9O$ radicals dissociate and form butenols/butanal, or smaller fragments including $CH_3$, $C_2H_4$, $C_2H_5$, $C_3H_6$, and enols (ethenol + propenol)
- $C_4H_9O$ radicals also react with other radical species, mainly H and O

**Relative Rate of Consumption:**

![Graph showing relative rate of consumption with various reactions labeled.]
**n-butanol:**

**Reaction Path Analysis – Enols and Aldehydes**

- **Mole Fraction Profiles:**
  - the model over-estimates the importance of enols (ethenol, propenol, and butenol)
  - with the exception of butanal, the importance of aldehydes is under-estimated

- **Relative Rates of Formation:**
  - butenol (CH₃CH₂CHCHOH) and butanal (CH₃CH₂CH₂CHO) are formed via H-abstraction reactions of the C₄H₉O radicals
Summary and Outlook

✓ Summary:
  - PI-MBMS is employed to study the isomeric composition of low-pressure flat flames fueled by
    \[ n\text{-butanol} \quad \text{iso-butanol} \quad \text{iso-butane} \quad \text{iso-butene} \]
  - mole fraction profiles are used to improve detailed chemical models
  - only \( n\)-butanol combustion chemistry discussed here in detail
    ✓ reaction path analysis reveals important fuel-consumption pathways and uncovers uncertainties for \( \text{C}_4\text{H}_9\text{O} \) radical reactions
  - for iso-butane and iso-butene combustion chemistry insights see Bin’s poster

✓ Outlook:
  - provide more experimental data for further model refinements
  - consolidate the different mechanisms under development
  - low-temperature oxidation chemistry in a jet-stirred reactor (with Y. Ju)