High-Pressure Kinetic Mechanisms for Hydrogen and Hydrogen Syngas

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Motivation

- Growing interest in computational engine design/testing
  - Fluid mechanics and kinetics sub-models

- $\text{H}_2$ and $\text{H}_2/\text{CO}$
  - Synthesis gas ($\text{H}_2/\text{CO}/\text{H}_2\text{O}/\text{CO}_2$) from coal/biomass gasification
  - Core sub-model for all fuels

- Advanced engine technologies → High $P$, low $T_f$
  - Modeling difficulties for flames

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Difficulty in predicting high-pressure flames

- Large variations among models
- None of the models capture pressure dependence across all conditions

What controls high-$P$/low-$T_f$ flames?

\[
\begin{align*}
H+O_2 &\rightarrow \text{OH}+\text{O} \quad \text{(R1)} \\
+M &\rightarrow \text{HO}_2 \quad \text{(R2)} \\
\end{align*}
\]

- More \(\text{HO}_2\) \\
  \(\rightarrow\) more \(\text{HO}_2\)+radical flux

- Flame zone shifts \\
  \(\rightarrow\) peak sensitivity at higher \(T\)'s \\
  \(\rightarrow\) collision efficiencies of products

- More R1/R2 competition \\
  \(\rightarrow\) amplified sensitivity

(Situation similar for \(\text{H}_2/\text{CO}\))

**Complexity of the modeling problem**

- Uncertainty in all reactions of 10% → burning rate uncertainty of 30%
- Realistic accuracy improvements for *elementary reactions* will not yield typical expected accuracies for *global behavior*
- Optimization against global targets necessary

![Sensitivity Coefficient](image)

- Functional temperature dependence of $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$ highly disputed/unknown
- Parameter optimization techniques don’t work if the *functional dependence* is not known

Complexity of the modeling problem

- A rigorous modeling solution will likely require **both**:
  - Empirical adjustments to rate constants
  - Improved fundamental understanding of select processes
- Neither alone appears sufficient to solve the problem.

Updated kinetic-transport models

- **H₂**: Hong et al. (2011) and Burke et al. (2012)*
  - HO₂ formation/consumption
    - H+O₂(+M) = HO₂(+M)
    - HO₂+radical reactions
  - H₂O₂ reactions
  - … among others

- **CO**: Haas et al. (2012)
  - CO + OH = CO₂ + H, CO + HO₂ = CO₂ + OH
  - HCO chemistry

*Uncertainties remained: adjustments of rate parameters to improve predictions*

Model performance

- Hong/Burke perform similarly well against most targets
- Largest differences in flames
  - Burke et al. – within 20%, Hong et al. – within 40%
- Parameter adjustments not unique → uncertainties remain!

Uncertainties remaining in 2012 (for flames)

- Parametric uncertainties
  - $\text{HO}_2 + X$ reactions
    - $\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$
    - $\text{H}_2 + \text{O}_2$
    - $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$
    - $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$

- $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$
  - Pressure dependence
  - 3rd body efficiencies for $\text{H}_2\text{O}$ and $\text{CO}_2$

- $\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$

- Model assumptions
  - Nonlinear mixture rules

Recall the complexity of the modeling problem and uncertainties in $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$

A rigorous modeling solution will likely require **both**:
- Empirical adjustments to rate constants
- Improved fundamental understanding of select processes

Neither alone appears sufficient to solve the problem.

Modeling strategies

- **Current kinetic models: sets of rate parameters**
  - Hierarchical, comprehensive modeling
    - Westbrook & Dryer (1984)
  - Optimization and Uncertainty Quantification
    - Turányi et al. (2012), Sheen et al. (2012): Uncertainty quantification of $A-n-E_a$
  - Require massive amounts of data to constrain full $T/P/M$-dependence of all $k$’s
    - Extrapolation outside the dataset very challenging

- **Direct incorporation of theory useful**
  - Replaces fitting formulas with physical theories
  - Common for extrapolation of data for a single reaction
  - Imposes constraints spanning all $T/P/M$

- **Multi-scale models: sets of molecular parameters**
  - Optimal use of information from *ab initio* calculations, $k$ measurements, combustion measurements
  - Theory *fills in the gaps* across all $T/P/M$

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\[ \text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2 \]

\( \text{(R1)} \quad \text{H}_2\text{O}_2(+\text{M}) = \text{OH} + \text{OH}(+\text{M}) \)

\( \text{(R2)} \quad \text{H}_2\text{O}_2 + \text{OH} = \text{HO}_2 + \text{H}_2\text{O} \)

\( \text{(R3)} \quad \text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2 \)

\( \text{(R4)} \quad \text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2 \)

\( \text{(R5)} \quad \text{OH} + \text{OH} = \text{O} + \text{H}_2\text{O} \)
Multi-scale informatics

*set of molecular parameters* informed by data across all scales

I. Molecular data

\[ E^†, \nu's, \nu_{imag}, \ldots \]

II. Rate constant measurements

\[ k_n(T,P,M) \]

III. Combustion measurements

\[ [OH] \text{ vs. } t, s_U, \ldots \]

Mathematical implementation

- Local “surrogate model”
- Least-squares error minimization
- Iterated until converged

\[
S_{ij} = \delta_{ij}
\]

\[
S_{ij} = \frac{\partial \ln k_{p,n}(T_i,P_i,M_i)}{\partial X_j}
\]

\[
S_{ij} = \sum_n \frac{\partial F_i}{\partial \ln k_{p,n}(T_i,P_i,M_i)} \frac{\partial \ln k_{p,n}(T_i,P_i,M_i)}{\partial X_j}
\]

\[
X_j = \text{Optimization parameters:}
\]

\[
\text{Molecular parameters} + \text{experimental conditions}
\]

\[
F_i(X_j) = Y_{i,i} \pm Z_i
\]

\[ \sum_j S_{ij} (X_j - \tilde{X}_j) = Y_i \pm Z_i \rightarrow X_{j,\text{opt}} \text{ and } C_X \]
Implementation for \( H_2O_2 \) system

**Optimization variables**

\[
\begin{align*}
H_2O_2(+M) &= OH+OH(+M) \\
H_2O_2+OH &= HO_2+H_2O \\
HO_2+HO_2 &= H_2O_2+O_2 \\
HO_2+OH &= H_2O+O_2 \\
OH+OH &= O+H_2O
\end{align*}
\]

**Optimization Targets**

I. Molecular data:

*ab initio* calculations (Klippenstein/Harding)

II. Rate constant measurements:

*see paper*

III. Combustion measurements:

\textbf{OH(t), H}_2\textbf{O(t)} \quad \textit{Shock-heated H}_2\textit{O}_2/\textit{Ar} (Hong et al. 2009,2010)

\textbf{OH(t)} \quad \textit{Shock-heated H}_2\textit{O}/\textit{O}_2/\textit{Ar} (Hong et al. 2010)

\textbf{abs}\text{215nm}(t) \quad \textit{Shock-heated H}_2\textit{O}_2/\textit{Ar} (Kappel et al. 2002)

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Different interpretations for OH+HO₂

Kappel et al. experiments
Kappel et al. predictions
A priori model
Constrained model

Much weaker T-dependence
(Secondary reactions)

Lower magnitude
(Arbitrary H atom doping)

Consistent description of $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$

- Single description consistent with:
  1. Ab initio calculations
  2. Low-$T$ $k$ measurements
  3. High-$T$ raw global data
- Milder $T$-dependence
  - Minimum near 1200 K

Consistent description of $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$

- *Simultaneous weighting* of diverse data types
- Theory guides experimental interpretations
- Raw data and careful documentation extremely powerful

Consistent description of $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$

Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson

“On the rate constants of $\text{OH} + \text{HO}_2$ and $\text{HO}_2 + \text{HO}_2$: A comprehensive study of $\text{H}_2\text{O}_2$ thermal decomposition using multi-species laser absorption.”

Combustion Symposium: 5D11

M.P. Burke, S.J. Klippenstein, L.B. Harding

“A quantitative explanation for the apparent anomalous temperature dependence of $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$ through multi-scale modeling.”

Combustion Symposium: 4D09

Conclusions

- High-pressure syngas flames
  - Emphasize HO$_2$ pathways + collision efficiencies of CO$_2$/H$_2$O
  - Inherently difficult to model

- Rigorous modeling solutions
  - Empirical adjustments based on global targets
  - Improved fundamental characterization

- Uncertainties remain in both 1) model parameters and 2) model assumptions

- Moving forward
  - Incorporation of theory to *fill in the gaps*
  - Raw data and careful documentation
  - Characterization of non-idealities/uncertainties in experiments and theory
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Thank you.

Questions?
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