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Updated H_2/O_2 Model to Address High-Pressure Flame Burning Rate Discrepancies

Michael P. Burke[1*], Marcos Chaos[2], Yiguang Ju[1], Frederick L. Dryer[1], Stephen J. Klippenstein[3]

[1]Princeton University, USA; [2]F.M. Global, USA; [3]Argonne National Laboratory, USA

mpburke@princeton.edu

http://www.princeton.edu/~combust

PrincetonUniversity
Mechanical & Aerospace Engineering Department

Introduction & Motivation

- Knowledge of the H_2/O_2 oxidation mechanism is a fundamental issue in combustion.
  - Accurate kinetic and transport models are necessary for computational design and optimization of gas turbine engines for syngas combustion as part of Integrated Gasification Combined Cycle processes.
  - H_2/O_2 chemistry is a core subset of all hierarchically developed hydrocarbon oxidation models.
- Most practical applications, particularly syngas combustion in GT engines, operate at high pressures (> 10 atm), frequently using lean conditions and/or dilution to lower flame temperatures to achieve low NO_x emissions.
- A number of recent studies [1-4] have revealed substantial difficulties in accurately predicting flame behavior at high pressures and low flame temperatures. None of the kinetic models predict the pressure dependence across all conditions (Fig. 1).
- The inability of presently available kinetic models to predict high-pressure, dilute flame behavior motivated us to update the H_2/O_2 model previously developed in our laboratory [5], with particular attention devoted to reactions sensitive in high-pressure flames (Fig.2).

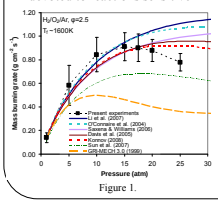


Figure 1.

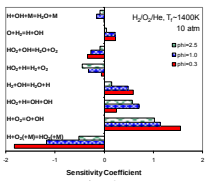


Figure 2.

Model Development

Processes/Reactions Revisited

- Present model uses the 19-reaction mechanism of Li et al. [5].
- Treatment of the following processes/reactions were revisited and in some cases revised as part of the present modeling study: $H+O_2(+M)=HO_2(+M)$, $H+HO_2$=products, $H+O_2=OH+O$, $O+H_2=OH+H$, $O+H_2O=OH+OH$, $H+OH+M=H_2O+M$, $HO_2+OH=H_2O+O_2$, $HO_2+O=O_2+OH$, $H_2O_2(+M)=OH+OH(+M)$, $OH+H_2O_2=H_2O+HO_2$, and H atom diffusion.

Potential "Missing" Reactions

- The effects of the following often-neglected reactions on predictions of the validation targets were tested using rate constants available in the literature: $H+HO_2+M=H_2O_2+M$, $O+OH+M=HO_2+M$, $H_2+O_2=OH+OH$, $H_2+O_2=H_2O+O$, $H_2O_2+O=H_2O+O_2$, $H+HO_2=H_2O+O$.
- A calculation performed using direct variable reaction coordinate TST as part of this study yields a rate constant for O+OH+M consistent with [6], the lower bound of proposed rate constants discussed by [2].
- The above reactions have negligible effect on validation set predictions with the exception of $H+HO_2=H_2O+O$ R3 (see $H+HO_2$=products section). The present model neglects R3 (consistent with use of lower proposed values for k_3 that make the reaction unimportant).

Approach

- For many combustion phenomena, sensitivities to fundamental kinetic parameters are so high that some of parameters must be adjusted to achieve reasonable accuracies in predictions.
- A more advanced optimization scheme is outside the scope of the present work, though we note that the updated model performs well when kinetic parameters for $H+HO_2=H_2+O_2$ and $H+O_2(+M)=HO_2(+M)$ are adjusted within uncertainties.
- Motivation for parameter adjustments is based on the premise that similar cancellations of errors will occur across a wider set of conditions than the existing validation set. We emphasize here that "validation" is a necessary but not sufficient condition for model accuracy across a wide range of conditions, though a more diverse validation set should yield a more accurate model over a wider range of conditions.
- Fig. 3 shows burning rate uncertainties associated with uncertainty in each elementary reaction rate constant estimated in [7]. Two of the best characterized reactions, the $H+O_2$ channels, have the largest contribution.

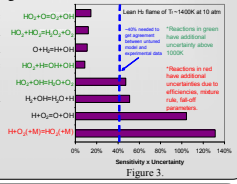


Figure 3.

Discussion Highlights

H + HO_2 = Products

- H + HO_2 reactions are among the most sensitive reactions in many combustion systems (H_2 and hydrocarbons alike).
- There are relatively few studies on the rate constants of the various channels, particularly at higher temperatures.
- The main channels are:
  - $H + HO_2 = OH + OH$ R1
  - $H + HO_2 = H_2 + O_2$ R2
  - $H + HO_2 = H_2O + O$ R3
- Reinterpretation of the k_1+k_3 and k_2 determinations of Baldwin & Walker [8] using better rate constants now available for ancillary reactions yield values lower by a factor of four from the originally proposed values.
  - Many models and rate assessments still based on original determination.
- Calculation using direct variable reaction coordinate TST as part of this study yields k_1 consistent with that used in Li et al. [5] within ~20%. Present model retains k_1 from [5].
- Present model uses k_2 proposed by Michael et al. [9] based on CTST theory calcs.
  - Consistent with low-T data [10-11], intermediate-T data [8] reinterpreted, and high-T data on reverse reaction [9].
- Role of R3 remains uncertain. Using k_3 values from [12] affects flow reactor speciation and high-pressure flames, while k_3 from [13] yields no effect.
- Further studies for all three channels at high temperature would be highly worthwhile for constraining model uncertainties.

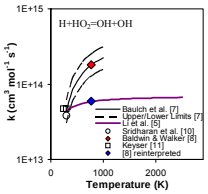


Figure 4.

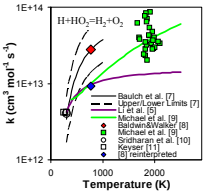


Figure 5.

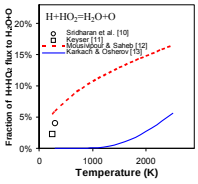


Figure 6.

Mixture Rules & Fall-off for $H+O_2(+M)=HO_2(+M)$

- At best, kinetic models assume a linear mixture rule for multi-component bath gases. At worst, the implementation of some kinetic models in CHEMKIN results in several times the high-pressure limit [14].
- Different components of a bath gas mixture "interact" in unimolecular/recombination reactions through modification of the reactant energy-state distribution, assuming at least one of the components is a weak collider (e.g. [15-16]).
- Our preliminary calculations yield trends (Fig. 7) that are consistent with earlier studies in the low-pressure limit, given that H_2O is a much stronger collider than Ar.
- Larger nonlinear interactions are observed when:
  - Components have different <ΔE>'s (with at least one component a weak collider).
  - Stronger collider is present is small mole fractions (~5 to 10%).
  - The reaction is in the intermediate fall-off range.
- Nonlinear interactions always increase the reaction rate [16]. Our calcs and those of [15] show nonlinearities of ~ 10%.
- Peak H consumption by $H+O_2(+M)$ in flames occurs near the post-flame zone where H_2O mole fraction is ~ 10% and nonlinear mixing effects are highest (Fig. 8).
- Fig. 9 compares flame predictions w/ and w/o nonlinear mixing effects estimated at ~10% – yielding 15% differences.
- Mixing interactions are highly dependent on <ΔE> values that are quite uncertain. Therefore, the accuracy of the present results and as such the role of nonlinear mixing effects is uncertain. At present, we have not attempted to include these effects in our kinetic model.

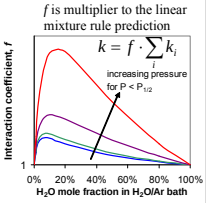


Figure 7.

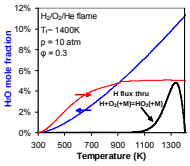


Figure 8.

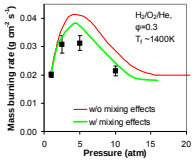


Figure 9.

Performance of Updated Kinetic-Transport Model

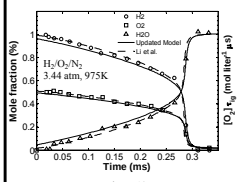
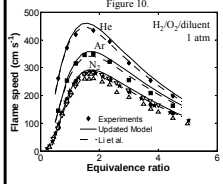


Figure 10.



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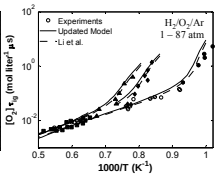


Figure 12.

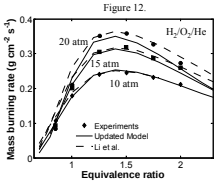


Figure 13.

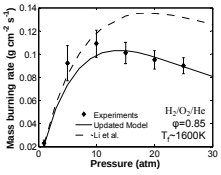
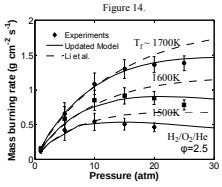


Figure 14.



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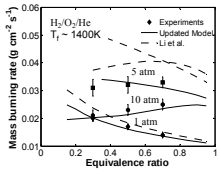

Figure 16.

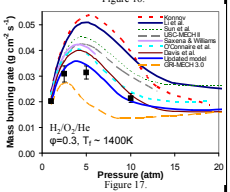

Figure 17.

- Reproduces previous validation targets of Mueller et al. [17] and Li et al. [5], including flow reactor speciation, ignition delays, and flame speeds, with reasonable agreement (though slightly reduced fidelity). Examples are shown in figures above. (References associated with experimental data shown can be found in [5]).
- Shows significant improvements against high-pressure, low-flame-temperature data of [1-2].
- Predicts flame speed targets of Refs. [1-2] and from [5] (spanning a wide range of equivalence ratios, pressures, diluents, and flame temperatures) within 20%.

Conclusions

- An updated kinetic model is constructed to incorporate recent improvements in rate constant determinations. Particular emphasis is placed on improving the treatment of reactions responsible for HO_2 production and consumption, which were found to be important in the flames studied in Refs. [1-4]. Most notably, we have considered various aspects of the treatment for $H+O_2(+M)=HO_2(+M)$ including mixture rules and fall-off behavior as well as HO_2+radical reactions.
- Given that uncertainties in combustion predictions stemming from uncertainties in the elementary rate constants were still prevalent, minor adjustments were made to maintain reasonable fidelity to previous validation targets as well as improve predictions against more recent high-pressure, low-flame-temperature flame speed data of interest to practical syngas applications and other advanced engine technologies.

Acknowledgments

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Authors

Michael Burke | Marcos Chaos | Yiguang Ju | Frederick Dryer | Stephen Klippenstein