Beyond Conventional Models: Implementation of LMR-R Framework for Multi-Collider Systems in Hydrogen Combustion

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Abstract

Recent advances enable precise parametrization of hydrogen combustion reaction rates, essential for zero-carbon energy applications. We implement Linear Mixture Rules in Reduced pressure (LMR-R) within OpenSMOKE++ to enhance prediction accuracy for six critical pressure-dependent reactions. Our methodology combines ab initio transition state theory with master equation solutions to determine collisional parameters across diverse conditions. Results reveal significant variability in energy transfer efficiencies among bath gas species. While our model agrees with experimental data under standard conditions, notable differences emerge in extreme environments like low-pressure oxycombustion. Sensitivity analyses show pressure-dependent termolecular reactions exhibit substantially different behaviors with advanced mixture rules versus conventional approaches. These findings help resolve disparities between microkinetic data and macroscopic combustion metrics, supporting hydrogen's integration in clean energy systems.

Introduction

Hydrogen is a key molecule for energy transition, but its implementation faces technical challenges requiring accurate predictive modeling. While conventional "pressure-dependent" reaction models like Lindemann or Troe formulations work for simple reactions, they inadequately characterize the complex multi-well, multi-channel systems in hydrogen combustion. These reactions are influenced by both pressure and bath gas composition, with varying collision properties between different species. This study implements the Reduced Pressure Based Linear Mixture Rules (LMR-R)[1] within OpenSMOKE++ to enhance mixture-dependent reaction rate predictions. We validate this through kinetic simulations using rate constants determined via ab initio transition state theory based master equation for six critical reactions in the H_2 sub-mechanism: R1) $2H(+M)=H_2(+M)$, R2) $2O(+M)=O_2(+M)$, R3) $H+O(+M)=OH(+M)$, R4) $H+OH(+M)=H_2O(+M)$, R5) $H+O_2(+M)=HO_2(+M)$, R6) $H_2O_2\ (+M)=2OH(+M)$.

Methodology

Combining theoretical calculations with experimental validation to develop accurate hydrogen combustion kinetics. High-pressure recombination fluxes were computed using TST, applying different approaches for atomic recombinations (reactions 1-3) versus more complex recombinations (reactions 4-6). Pressure-dependent rate constants are determined through ME simulations using MESS software, which estimates two critical parameters for each bath gas species: collision efficiency (α) and average energy transferred per downward collision ($\langle \Delta E \rangle_{down}$). These parameters are optimized by fitting to experimental measurements across temperatures of 250-2500K and pressures of 0.001-100 atm. For some diatomic reactions, consistently fitting experimental data required additional corrective parameters to address limitations in the energy transfer model. The calculated rate constants were then parametrized in PLOG format for each collider and reaction. To improve upon conventional mixture models, we implemented the Linear Mixture Rule in Reduced pressure (LMR-R)[1] framework within OpenSMOKE++. This approach maintains accuracy within approximately 10-20% across diverse conditions while properly accounting for bath gas mixture effects that conventional models inadequately represent.

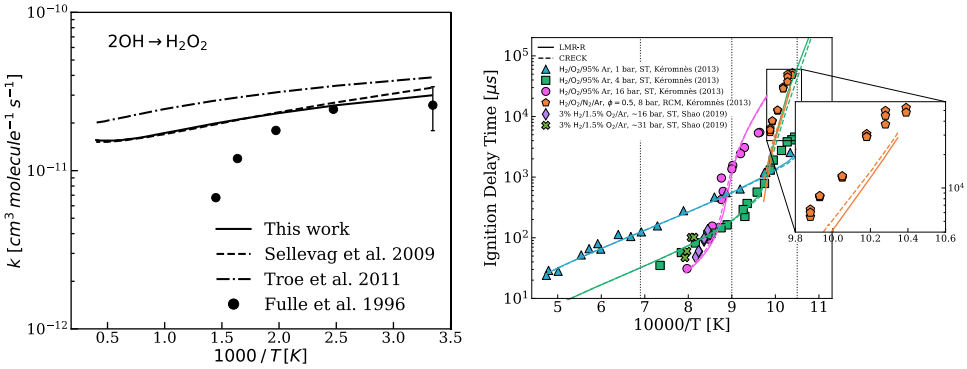

Figure1. Left panel: High Pressure Limit OH+OH recombination here calculated and the theoretical estimation of [2], experimental measurements from[3,4]. Right panel: Ignition delay times calculations with LMR-R (solid) and CRECK (dashed) models against experimental measurements [5,6].

Results and discussion

Our theoretical rate constant calculations for H_2 combustion reactions show excellent agreement with prior advanced studies. For example, our high-pressure limit rate constant for OH+OH recombination aligns well with Sellevåg's theoretical predictions and Troe's proposed values Fig. 1(left). This validates our computational approach for both recombination and decomposition processes. Collisional parameters determined through systematic regression against experimental data (850

total measurements) revealed significant variations in energy transfer efficiencies among different bath gas species. The average energy transferred per downward collision ($\langle\Delta E\rangle_{down}$) ranged from 130-200 cm^{-1} for weak colliders to 3000-4000 cm^{-1} for strong colliders. Temperature dependence of these parameters also varied considerably (α from 0.35 to 1.02), with strong colliders consistently showing larger temperature dependencies. Our ME simulations uncovered some limitations in the single exponential down model. For certain reactions (especially R2 and R3), we observed unexpectedly efficient collisional energy transfer requiring correction factors in the density of states evaluations. This reveals fundamental challenges in accurately representing energy transfer processes even with advanced modeling techniques. When implemented in the CRECK framework, our enhanced hydrogen combustion mechanism showed interesting behavior during validation testing. While standard conditions showed good agreement with experimental data, notable improvements emerged under extreme environments, particularly in oxycombustion at reduced pressures (0.1-0.3 atm) where bath gas effects become more pronounced. Sensitivity analyses revealed that pressure-dependent termolecular reactions, especially $H+O_2(+M)=HO_2(+M)$, exhibit substantially different sensitivities when modeled with advanced mixture rules compared to conventional approaches. This work demonstrates that accurate parametrization of pressure and mixture-dependent rate constants can help resolve persistent disparities between microkinetic data and macroscopic combustion metrics, particularly in extreme or unconventional combustion conditions relevant to hydrogen's integration as a clean energy carrier.

References

[1] L. Lei, M. P. Burke, “Mixture rules and falloff are now major uncertainties in experimentally derived rate parametersfor $H+O_2(+M)=HO_2(+M)$”, Combustion and Flame 213 (2020) 467–474.

[2] S. R. Sellevag, Y. Georgievskii, J. A. Miller, “Kinetics of the gas-phase recombination reaction of hydroxyl radicals to form hydrogen peroxide”, The Journal of Physical Chemistry A 113 (16) (2009) 4457–4467.

[3] J. Troe, V. G. Ushakov, “SACM/CT Study of the dissociation/recombination dynamics of hydrogen peroxide on an ab initio potential energy surface Part II. Specific rate constants k(E,J), thermal rate constants $k_\infty(T)$, and lifetime distributions”, Phys. Chem. Chem. Phys. 10 (26) (2008) 3915–3924.

[4] D. Fulle, H. F. Hamann, H. Hippler, J. Troe, “High-pressure range of the addition of HO to HO. III. Saturated laser-induced fluorescence mea- surements between 200 and 700 K”, The Journal of Chemical Physics 105 (3) (1996) 1001–1006.

[5] A. Keromnes, W. K. Metcalfe, K. A. Heufer, N. Dono- hoe, A. K. Das, C.-J. Sung, J. Herzler, C. Naumann, P. Griebel, O. Mathieu, M. C. Krejci, E. L. Petersen, W. J. Pitz, H. J. Curran, “An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures”, Combustion and Flame 160 (6) (2013) 995–1011.

[6] J. Shao, R. Choudhary, A. Susa, D. F. Davidson, R. K. Hanson, “Shock tube study of the rate constants for $H+O_2+M \rightarrow HO_2+M(M=Ar,H_2O,CO_2,N_2)$ at elevated pressures”, Proceedings of the Com- bustion Institute 37 (1) 2019) 145–152.