

How to improve kinetic mechanism for hydrogen combustion

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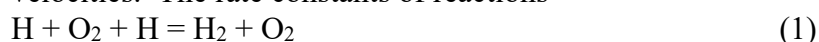
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Introduction

An analysis of all available burning velocity measurements of hydrogen flames using the heat flux method at atmospheric pressure [1] revealed that many experiments performed in several laboratories with different types of dilution by various inerts are consistent and thus highly valuable for validation of detailed kinetic mechanisms. Some experimental datasets, however, were identified as outliers and these conditions were revisited experimentally. New measurements [1] were found in agreement with the bulk of the data thus identifying couple studies where experimental uncertainties were probably underestimated.

The analysis of the data consistency [1] was guided by kinetic modeling using two kinetic mechanisms. The ELTE mechanism developed by Varga et al. [2] using an optimization approach showed a very good performance in predicting laminar burning velocities of hydrogen flames measured using the heat flux method. On the contrary, the Konnov [3] mechanism systematically overpredicted these burning velocities at most of the conditions tested. It was also noted that rate constants implemented in this mechanism [3] are only marginally different from those obtained during optimization of hydrogen [4] or syngas [2] combustion mechanisms. Still the discrepancy between predictions of the Konnov [3] mechanism and consistent datasets of experimental data for laminar burning velocities was a strong motivation for search and analysis of the remaining deficiencies in the kinetic model of the author.

A possible resolution of this problem was indicated by Burke and Klippenstein [5, 6] who proposed that “chemically thermolecular” reactions in conditions of high concentrations of H atoms and other radicals may constitute major kinetic pathways affecting laminar burning velocities. The rate constants of reactions



have been calculated by Burke and Klippenstein [6] who demonstrated that inclusion of them into detailed kinetic models significantly reduces predicted burning velocities of $\text{H}_2 + \text{air}$ and $\text{H}_2 + \text{O}_2 + \text{He}$ flames. The importance of this class of reactions was discussed and emphasised, and apparently they are not limited to the recombination of H atoms and oxygen [7]. Straightforward addition of reactions (1) – (4) to the Konnov [3] mechanism, however, does not improve the model performance for $\text{H}_2 + \text{air}$ flames as shown in Fig. 1. The calculated burning velocities become significantly lower than the measurements of Krejci et al. [8], which are considered to be one of the most reliable dataset for model validation [3, 9]. Note that for these hydrogen flames the predictions of the Konnov [3] mechanism are very close to those of the ELTE mechanism [2] over entire range of equivalence ratios, ϕ , with only minor differences in lean mixtures illustrated elsewhere [1]. Therefore the goal of the present study was to revisit other parameters of the kinetic mechanism for hydrogen combustion in attempt of improving its accuracy while including chemically thermolecular reactions.

Rate constants

Analysis of the recent experimental and theoretical kinetic studies of hydrogen reactions was performed and three rate constants were updated. New expressions for the rate constants of

reactions $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ [10, 11] and $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ [12] are very close to the previously implemented. Modifications do not exceed 10-20 % and should not affect model performance for self-ignition, slow oxidation and flame propagation that was also tested. The rate constant of reaction $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$ (1Δ) was modified dramatically, accepting theoretical calculations of Monge-Palacios and Sarathy [13], however, according to the authors, this change does not affect model predictions for thermal combustion of hydrogen. Furthermore, sensitivity analysis of the burning velocity of $\text{H}_2 + \text{air}$ flame revealed that new reaction (1) $\text{H} + \text{O}_2 + \text{H} = \text{H}_2 + \text{O}_2$ has the highest negative sensitivity coefficient. Therefore the focus of the further search on how to counterbalance enhanced chain termination caused by chemically termolecular reactions and validation of the updated model was on flame propagation.

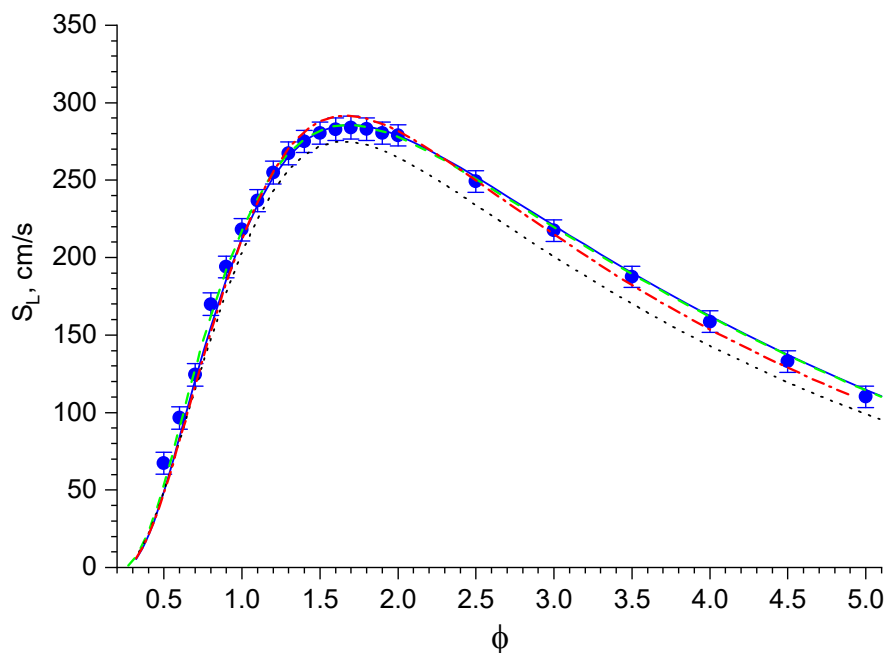


Fig. 1. Laminar burning velocity of $\text{H}_2 + \text{air}$ flames at atmospheric pressure. Symbols: experiments [8], lines: modeling. Solid blue: ELTE [2], dashed green: Konnov [3], black dot line: include chemically termolecular $\text{H} + \text{O}_2$ reactions (1) – (4), dash-dot red line: present model.

Transport parameters

Transport parameters are an integral part of any kinetic mechanism required for modeling non-uniform processes such as flame propagation. It was realized long ago that transport properties are as important in flame modeling as rate constants of chemical reactions [14, 15]. Some 40 years ago several computer codes for flame modeling were developed adopting 12-6 Lennard-Jones potential to calculate diffusion coefficients [16], and a common database was established. This database originating from Sandia National Laboratories was made popular together with widely used Chemkin package [17], and implemented in numerous kinetic mechanisms including GRI-mech and optimized models for hydrogen [4] or syngas [2] among many others.

Recent theoretical studies showed that in many cases quantum scattering calculations of diffusion coefficients significantly deviate from those using 12-6 Lennard-Jones potential at high temperatures typical to flames. Furthermore, implementation of these updated diffusion coefficients leads to notable increase of the calculated burning velocities for hydrogen and methane flames [18]. Flame modeling using binary diffusion coefficients from ab initio calculations requires modifications in the transport routines of Chemkin as suggested by Wang

and colleagues [19, 20] that can be realized with original Chemkin-II Fortran codes, not with Chemkin-Pro [17]. This does not mean, however, that classical 12-6 Lennard-Jones potential should not be used to calculate diffusion coefficients.

Jasper et al. [21, 22] created a new transport database suitable for direct use with Chemkin. Transport parameters for many individual molecules and radicals in nitrogen $A+N_2$ were calculated. Then the pure gas $A+A$ parameters were obtained by reversing the combining rules using the computed values for N_2+N_2 . This database is adopted in the present model without modifications. Transport parameters for excited species $O(1D)$ and $OH(^2\Sigma^+)$ were assumed equal to O and OH , respectively.

Results and discussion

A combination of the new and updated reactions and transport database developed by Jasper et al. [21, 22] constitutes a new kinetic model for hydrogen combustion. These modifications mostly affect calculated burning velocities, as shown in Fig. 1. The new model accurately reproduces burning velocities of $H_2 + \text{air}$ flames both in lean and rich mixtures with slight overprediction in close to maximum values, yet within the uncertainties of the measurements [8]. Remarkably, the theoretical transport data [21, 22] counterbalance enhanced chain termination caused by chemically termolecular reactions [5, 6] and restore originally good performance of the Konnov [3] mechanism for hydrogen flames burning in air. Moreover, at all experimental conditions previously scrutinized by Alekseev and Konnov [1] the new model closely approaches predictions of the ELTE [2] optimized mechanism.

Conclusions

Present study demonstrates that incorporation of the chemically termolecular reactions $H + O_2 + R$ suggested by Burke and Klippenstein [5, 6] into kinetic mechanisms is not only necessary and possible, but actually improves the model performance if accompanied by the updates in the transport properties implemented in the flame modeling. When these reactions are included alone they affect global reactivity and significantly reduce calculated burning velocities of laminar premixed flames.

It was found that implementation of the new theoretical transport database developed by Jasper et al. [21, 22] significantly improves the performance of the updated kinetic model. The new kinetic mechanism for hydrogen combustion which includes updated kinetics and new transport properties was found in good agreement with consistent dataset of the burning velocity measurements for hydrogen flames obtained using the heat flux method at atmospheric pressure for which the behavior of the previous model of the author was not satisfactory.

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