



Yet another kinetic mechanism for hydrogen combustion

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ABSTRACT

Recent suggestion by Burke and Klippenstein (2017) that chemically termolecular reactions $H + O_2 + R$ may significantly affect kinetic pathways under common combustion situations requires careful analysis, since, if included in contemporary kinetic mechanisms, these reactions affect global reactivity and calculated burning velocities of laminar premixed flames. In the view of their impact, a detailed kinetic scheme for hydrogen combustion was revisited to elucidate how to counterbalance enhanced chain termination caused by chemically termolecular reactions in attempt to keep or improve model performance. First, recent experimental and theoretical kinetic studies of hydrogen reactions were analyzed. In the new mechanism four reactions were introduced and three rate constants were updated. These changes, however, significantly reduce calculated burning velocities of $H_2 + \text{air}$ flames as compared to experimental data and earlier model predictions with the major impact from chemically termolecular reactions. It was then found that implementation of the new theoretical transport database developed by Jasper et al. (2014) 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 the 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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1. 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 termolecular” 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 $H_2 + \text{air}$ and $H_2 + O_2 + \text{He}$ flames. The importance of this class of reactions was discussed and emphasised [7], and apparently they are not limited to the recombination of H atoms and oxygen [8]. Straightforward

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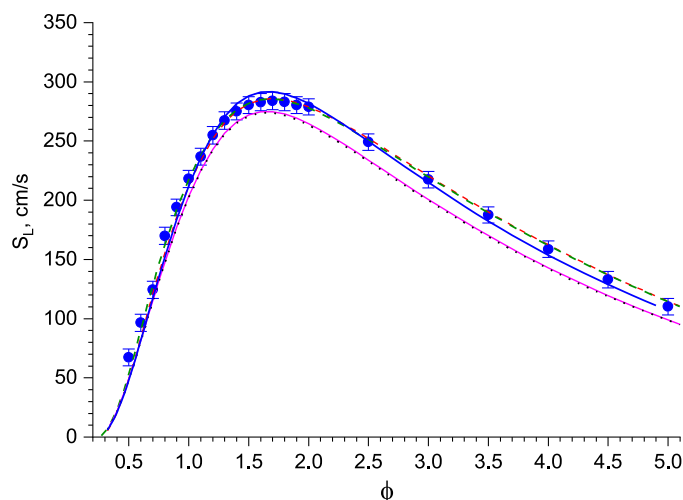


Fig. 1. Laminar burning velocity of H_2 + air flames at atmospheric pressure. Symbols: experiments [9], lines: modeling. Red dashed: ELTE [2], green dashed: Konnov [3], solid magenta: include chemically termolecular $\text{H} + \text{O}_2$ reactions (1)–(4), black dot line: all reactions included, solid blue line: present model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

addition of reactions (1)–(4) to the Konnov [3] mechanism, however, does not improve the model performance for H_2 + air flames as shown in Fig. 1. The calculated burning velocities become significantly lower than the measurements of Krejci et al. [9], which are considered to be one of the most reliable datasets for model validation [3,10]. 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 termolecular reactions.

2. Modeling details

For calculations of the burning velocity, PREMIX code of Chemkin-Pro [11] was used. The modeling was performed with multicomponent transport coefficients and thermal diffusion option. Adaptive mesh parameters were $\text{GRAD} = 0.012$ and $\text{CURV} = 0.1$ for the free propagating model, resulting in a typical number of grid points around 700.

3. Rate constants

During recent years since the development of the previous hydrogen kinetic model in 2015 [3] several studies contributed to better and more accurate understanding of combustion chemistry of hydrogen. For instance, reaction $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$ has been investigated theoretically [12–14] and very good agreement with earlier experimental studies was found. The difference between calculated rate constants, however, is larger than the difference between rate constants implemented in the mentioned models [2–4] as presented and discussed in [1], which hampers selection of the most appropriate updated expression for this reaction.

Experimental study of reaction



from 295 to 701 K [15] not covered in the development of the hydrogen kinetic mechanism [16], indicated that the rate con-

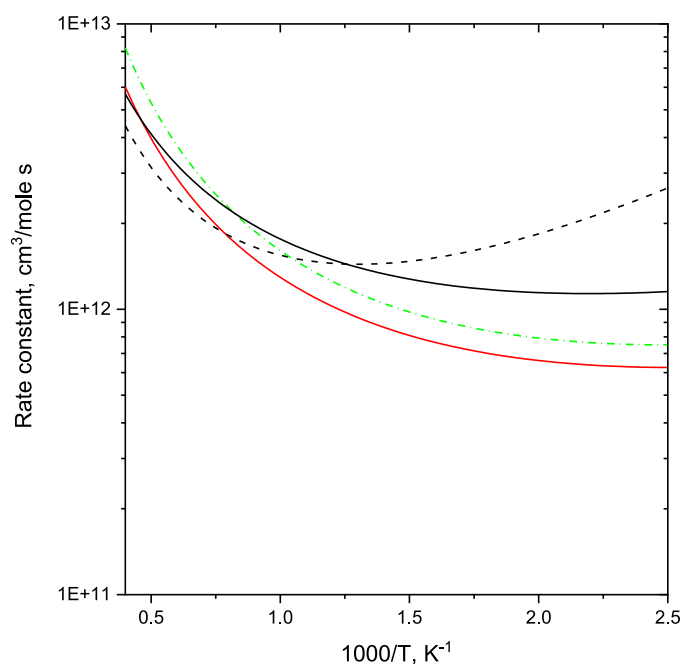
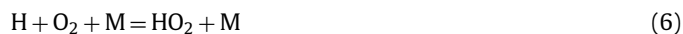


Fig. 2. Rate constants of reaction $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$. Red solid line: optimized syngas mechanism [2], black dashed line: optimized hydrogen mechanism [4], dash-dot green line: Konnov mechanism [3], black solid line: updated rate constant [15]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stant obtained by Sangwan and Krasnoperov [17] below 834 K is lower than other measurements. Moreover, the low-temperature rate constant [15] was found in excellent agreement with the theoretical work of Nguyen and Stanton [18]. Altinay and Macdonald [15] proposed a fit to the theoretical results [18] and showed that it is in very good agreement with high-temperature measurements of Wooldridge et al. [19] and with reverse rate constant derived from the data of Sutherland et al. [20]. Also Hong et al. [21] supported results of Wooldridge et al. [19] in their shock-tube study of H_2O_2 decomposition. Figure 2 depicts rate constants implemented in the previous models [2–4] as well as the new expression [15] adopted in the present work. Note that the rate constant of Baulch et al. [22] used in [3] is very close to the expressions based on the studies of Wooldridge et al. [19] and Sutherland et al. [20] at high temperatures as discussed by Alekseev et al. [16].

New measurements became available for the key chain-branching reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ over the temperature range 1428–1520 K [23]. Excellent agreement was found with the previous data reported by Hong et al. [24]. The rate expression proposed [24] covers extended temperature range of 1100–3370 K since it includes earlier data of Masten et al. [25]. It was therefore selected by Alekseev et al. [16] and kept unchanged in the present study.

Shao et al. [26] measured ignition delays of $\text{H}_2 + \text{O}_2 + \text{Inert}$ mixtures and derived low-pressure rate constants of recombination



for Ar, H_2O , CO_2 and N_2 . Ignition delays strongly depend on the ratio of rates of recombination and chain branching $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, for which the rate constant of Wang et al. [23] and Hong et al. [24] was used. Low-pressure rate constants for each bath gas were derived using high-pressure limiting rate constant of Troe [27] and the same temperature dependence was suggested. This facilitates implementation of this reaction in combustion codes since it avoids multiplication of the total rate constant by the number of separate expressions for each collider while approach-

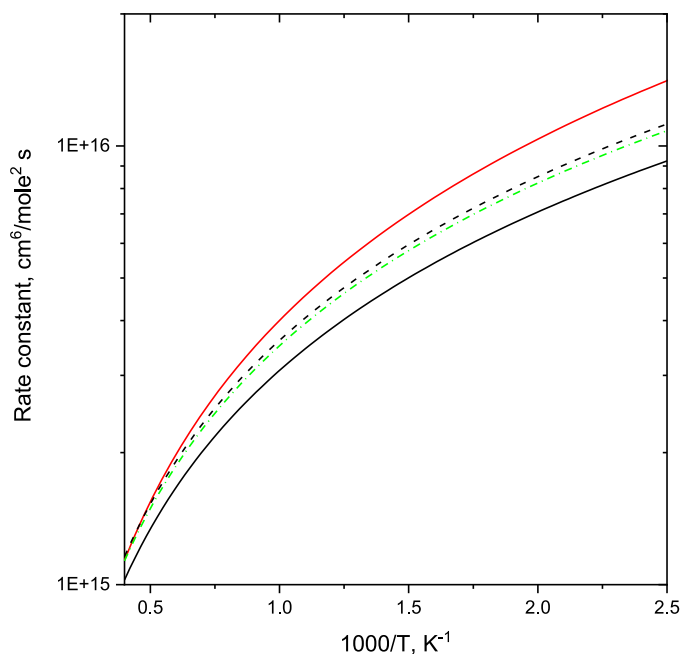


Fig. 3. Rate constants of reaction $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$. Red solid line: optimized syngas mechanism [2], black dashed line: optimized hydrogen mechanism [4], dash-dot green line: Konnov mechanism [3], black solid line – updated rate constant [26]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ing high-pressure limit. Although this problem may arise only at very high pressures of the order of 100 atm as discussed by Hong et al. [28] and accepted by Alekseev et al. [16], single reaction presentation with different collisional efficiencies allows for comprehensible sensitivity and reaction path analyses. The rate constant of Shao et al. [26] is adopted in the present model even though this presentation does not resolve the issue of the “mixture rules” discussed by Burke and Song [29]. The rate constants of reaction $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ implemented in the previous models [2–4] do not deviate significantly from the new expression as shown in Fig. 3.

Reaction between OH and HO_2 radicals is usually included in kinetic mechanisms as $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$. At low temperatures typical for atmospheric chemistry, formation of clusters with water may affect the rate of this reaction [30], which, however, is considered negligible for combustion. Role of recombination channel $\text{OH} + \text{HO}_2 + \text{M} = \text{HOOH} + \text{M}$ was analyzed by Badenes et al. [31] and found irrelevant at all conditions and pressures up to 400 atm. Recent rate constant measurements at room temperature [32] were attributed to reaction $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$ and found in good agreement with previous measurements of, e.g., Keyser [33]. Reaction between OH and HO_2 radicals can take place also on singlet potential energy surface forming singlet $\text{O}_2(\text{a}^1\Delta\text{g})$:



It was therefore included in the Konnov [3] mechanism with the rate constant calculated by Gonzalez et al. [34] aiming at analysis of possible role of ozone and reactions of excited species $\text{O}(1\text{D})$, $\text{OH}(^2\Sigma^+)$, and $\text{O}_2(\text{a}^1\Delta\text{g})$, in hydrogen combustion. Recently, Monge-Palacios and Sarathy [35] repeated ab initio calculations of this reaction at higher level of theory. Their rate constant for the triplet channel is within a factor of two of the rate constant derived by Hong et al. [36] and implemented in the previous [3] and present models, with expression proposed by Burke et al. [37], and with the rates obtained during optimization of hydrogen

[4] and syngas [2] mechanisms as illustrated in Fig. S1 of the Supplemental material. The rate constant for the singlet channel, however, was found [35] several orders of magnitude higher than that of Gonzalez et al. [34] as shown in Fig. S2 of the Supplemental material. Nevertheless Monge-Palacios and Sarathy [35] did not find an impact of this reaction on thermal combustion of hydrogen; small difference was seen only in the calculated burning velocities of the mixtures seeded with O_3 . This new rate constant of reaction (7) is adopted in the present mechanism.

Initiation in contemporary kinetic models for hydrogen combustion is commonly presented as reaction $\text{H}_2 + \text{O}_2 = \text{H} + \text{HO}_2$. Monge-Palacios and Rafatijo [38] investigated possible role of termolecular reactions $\text{O}_2 + \text{O}_2 + \text{H}_2 = \text{HO}_2 + \text{HO}_2$ and $\text{O}_2 + \text{O}_2 + \text{H}_2 = \text{H} + \text{HO}_2 + \text{O}_2$ and found their role possible only at very high pressures of the order of 3000 atm. Reverse of the initiation reaction can produce singlet oxygen $\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2(1\Delta)$ which slightly modifies pathways of hydrogen combustion at some specific conditions, e.g. in a flow reactor oxidation as revealed and discussed elsewhere [3]. Recently Pelevkin et al. [39] performed ab initio analysis of reactions of H_2 with O_2 in excited electronic states and concluded that their calculated rate constant of reaction $\text{H}_2 + \text{O}_2(1\Delta) = \text{H} + \text{HO}_2$ is in reasonable agreement with available experimental data. This rate constant is very close to the expression derived by Konnov [3] at around 2000 K while significantly lower at 1000 K, as illustrated in Fig. S3 of the Supplemental material. Pelevkin et al. [39] noted that their treatment of tunneling could not be accurate at low temperatures, that may lead to underestimation of the rate constant by orders of magnitude at 300 K, that is at conditions of all experimental kinetic studies. Therefore the rate constant of reaction $\text{H}_2 + \text{O}_2(1\Delta) = \text{H} + \text{HO}_2$ [3] is kept unchanged in the present mechanism.

Kinetic role of excited species $\text{O}(1\text{D})$ and $\text{OH}(^2\Sigma^+)$ in the thermal combustion of hydrogen was found negligible [3], thus modifications of the pertinent rate constants should not affect the model performance. Nevertheless, it is noteworthy that the rate constant of reaction $\text{H} + \text{O} + \text{M} = \text{OH}^* + \text{M}$ from Kathrotia et al. [40] selected in the Konnov [3] mechanism was recently confirmed in [41] as the most suitable for OH^* modelling.

Table 1 lists newly incorporated chemically termolecular reactions and reactions with updated rate constants. These modifications altogether do not appreciably modify the mechanism performance in predicting hydrogen self-ignition and oxidation in a flow reactor. Several examples of the validation are presented in the Supplemental material. Olm et al. [42] compared the performance of many recent kinetic models for hydrogen and concluded that the model of Keromnes et al. [43] is overall the best. Therefore in our previous studies [3,16] and in the Supplemental material the present updated kinetic model is compared to the predictions of the mechanisms of Keromnes et al. [43] and of Konnov [3]. All three models are in a good agreement with ignition delays measured in a rapid compression machine by Mittal et al. [44]; the difference over 15–50 bars does not exceed 10–15%, see Fig. S4. Figure S5 presents experimental data on ignition delay times of $\text{H}_2 + \text{O}_2 + \text{Ar}$ mixtures in a shock tube at pressures 1–16 atm from the study of Keromnes et al. [43] with similar behavior of the models tested. Figures S6–S10 show simulations of the flow reactor data of Mueller et al. [45]. In lean mixtures the present model predictions are almost indistinguishable from those of the mechanisms of Keromnes et al. [43] and of Konnov [3] from low (Figs. S6 and S8) to high (Fig. S7) pressures. However, in stoichiometric mixtures (Figs. S9 and S10) the present mechanism shows lower reactivity compared to the other two models. A sensitivity analysis performed for oxidation of a stoichiometric mixture ($\text{H}_2=0.95\%$, $\text{O}_2=0.49\%$, N_2 balance) at 3.02 atm and initial temperature of 934 K revealed the same sensitive reactions as observed for the previous model and discussed in detail in [3]. No impact of the up-

Table 1

New and updated reactions in the H/O kinetic mechanism, units are $\text{cm}^3 \cdot \text{mole}^{-1} \cdot \text{s}^{-1} \cdot \text{cal}^{-1} \cdot \text{K}$, $k = AT^n \exp(-E_a/RT)$. UF – uncertainty factor.

No	Reaction	A	n	E _a	T range, K	UF	Source
1	$\text{H} + \text{O}_2 + \text{H} = \text{H}_2 + \text{O}_2$	$8.80\text{E}+22$	-1.835	800	300–3000	2	[6]
2	$\text{H} + \text{O}_2 + \text{H} = \text{OH} + \text{OH}$	$4.00\text{E}+22$	-1.835	800	300–3000	2	[6]
3	$\text{H} + \text{O}_2 + \text{O} = \text{OH} + \text{O}_2$	$7.35\text{E}+22$	-1.835	800	300–3000	2	[6]
4	$\text{H} + \text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$	$2.56\text{E}+22$	-1.835	800	300–3000	2	[6]
5	$\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$	$2.668\text{E}+06$	1.82	-1647	200–2000	1.4	[15,18]
6	$\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$	$4.66\text{E}+12$	0.44	0	300–2000	1.2	[27]
	Low pressure limit:	$1.225\text{E}+19$	-1.2	0.0	1000–1430	1.2	[26]
	F _{cent} = 0.5						
	Enhanced third-body efficiencies (relative to N ₂):						
	Ar = 0.72, H ₂ O = 16.6, CO ₂ = 3.61,						[26]
	He = 0.57, H ₂ = 1.5						[3]
7	$\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$ (1Δ)	$2.14\text{E}+06$	1.65	2180	200–2500	2	[35]

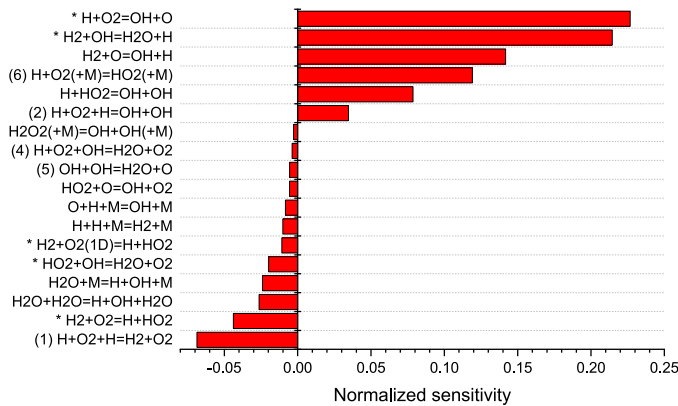


Fig. 4. Normalized sensitivities of the burning velocity of stoichiometric H₂ + air flame.

dated rate constants of reactions (5) and (7) was found; the role of reactions (1)–(4) was found negligible. One may conclude that chemically termolecular reactions (1)–(4) are not important during induction period of self-ignition or in the slow oxidation in a flow reactor due to much lower concentrations of radicals as compared to flames.

Implementation of all reactions listed in Table 1 lead to very small modification of the calculated burning velocities of H₂ + air flames compared to the case of addition reactions (1)–(4) only, as illustrated in Fig. 1. Sensitivity analysis performed for this updated mechanism in stoichiometric flame at atmospheric pressure is shown in Fig. 4. Reactions discussed above are marked with asterisk or with reaction number from Table 1. Remarkably, new reaction (1) has the highest negative sensitivity coefficient; also present are reactions (2) and (4). Note that other reactions manifested in the sensitivity spectrum all possess very close or the same rate constants across different kinetic schemes assessed by Alekseev et al. [16]. In that comparative study it was noted that contemporary hydrogen combustion mechanisms share the same thermodynamic data from the database of Goos et al. [46], while transport parameters could be different. This issue is analyzed in the following.

4. 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 chemi-

cal reactions [47,48]. Some 40 years ago several computer codes for flame modeling were developed adopting 12-6 Lennard-Jones potential to calculate diffusion coefficients [49], and a common database was established. This database originating from Sandia National Laboratories was made popular together with widely used Chemkin package [11], and implemented in numerous kinetic mechanisms including GRI-mech and optimized models for hydrogen [4] or syngas [2] among many others. Paul and Warnatz [49] in 1998 pointed out that this database is outdated and also that repulsive part of the Lennard-Jones potential should be described differently. Since then several solutions to this problem have been proposed, e.g., [49–51] as summarized and analyzed by Brown et al. [52]. Middha et al. [50] demonstrated that transport routines of Chemkin underpredict diffusion coefficients as compared to first-principle calculations. Dong et al. [51] emphasized that transport properties are very important in predicting extinction phenomena in premixed flames, and performed ab initio calculations of binary diffusion coefficients focusing on the properties of atomic and molecular hydrogen. Further progress was achieved through measurements of binary diffusion coefficients [53–55] and extensive ab initio calculations, e.g., [56–61]. Brown et al. [52] noted that experimentally determined diffusion coefficients for OH, HO₂, and ozone [53] yield improved description of diffusion at least for OH. Therefore the Lennard-Jones parameters proposed by Ivanov et al. [53] were adopted in the mechanisms of Alekseev et al. [16] and Konnov [3]. The theoretical studies [56–61] 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 [58].

Flame modeling using binary diffusion coefficients from ab initio calculations requires modifications in the transport routines of Chemkin as suggested by Wang and colleagues [50,51] that can be realized with original Chemkin-II Fortran codes, not with Chemkin-Pro [11]. This does not mean, however, that classical 12-6 Lennard-Jones potential should not be used to calculate diffusion coefficients. Jasper et al. [62,63] created a new transport database suitable for direct use with Chemkin. Transport parameters for many individual molecules and radicals in nitrogen A+N₂ were calculated. Then the pure gas A+A parameters were obtained by reversing the combining rules using the computed values for N₂+N₂. This database is adopted in the present model without modifications. Transport parameters for excited species O(1D) and OH(²Σ⁺) were assumed equal to O and OH, respectively, while for excited oxygen molecules O₂ (1Δ) were taken from the calculations of Pineda and Chen [64].

5. Results and discussion

A combination of the new and updated reactions listed in Table 1 and transport database developed by Jasper et al. [62,63] constitutes a new kinetic model for hydrogen combustion available in the Supplemental material. These modifications mostly affect calculated burning velocities, as shown in Fig. 1 (zoom out in Fig. S11 in the Supplemental material). The new model accurately reproduces burning velocities of H_2 + air flames both in lean and rich mixtures with slight overprediction in close to maximum values, yet within the uncertainties of the measurements [9]. Remarkably, the theoretical transport data [62,63] 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.

In the following the new model is validated against the measurements from consistent dataset obtained using the heat flux method at atmospheric pressure [1] for which the behavior of the previous model [3] was not satisfactory. Note that some measurements were found highly uncertain or inconsistent and therefore they are not shown in the following figures. Specifically, the measurements of Goswami et al. [65] in the mixture of 85:15 (H_2 + N_2) fuel with 12.5:87.5 (O_2 + He) oxidizer were found [1] probably erroneous due to equipment malfunction of their high-pressure installation. It was also concluded that the first measurements of the burning velocity in H_2 + O_2 + N_2 mixtures using the heat flux method by Hermanns et al. [66] are notably higher than those of subsequent studies due to rather simplified analysis of experimental uncertainties as compared to the procedures developed during recent years [67]. Kishore et al. [68] measured burning velocities in the mixtures (H_2 + O_2) + Inert for N_2 and Ar as diluents; however experimental uncertainties were not quantified in that study. Finally, Voss et al. [69] investigated fuel mixtures containing H_2 diluted by N_2 from 50 to 80% with air as an oxidizer. Eckart et al. [70] revisited some of these mixtures with dilutions of 70, 75 and 80% and extended the dilution up to 82%. These datasets obtained in the same laboratory [69,70] revealed some outliers [1], while some series possess too high uncertainties and therefore are not used here for model validation. In the following, agreement or disagreement with predictions of the models tested is discussed taking into account uncertainties of the measurements.

Burning velocity in lean H_2 + air flames at atmospheric pressure and initial gas temperature of 298 K measured using the heat flux method by Alekseev et al. [71] are presented in Fig. 5. Also shown are results obtained in spherical flames [72,73] and in counterflow flames [74–76] using non-linear methods (NLM) for stretch corrections which were considered to be the most reliable measurements at these conditions [10,71]. Significant scatter in the experimental data obtained with different methods prevents from conclusive preference of the Konnov [3], ELTE [2], or the present model. On the other hand only optimized mechanism of Varga et al. [2] and the present new one agree with the heat flux measurements of Alekseev et al. [71] and with the results obtained by Varea et al. [72] in spherical flames using a so-called direct method.

In addition to lean flames of H_2 + air covering the range of equivalence ratios from 0.4 to 0.5 shown in Fig. 5, Alekseev et al. [71] investigated reference mixtures with O_2 + N_2 oxidizer dilution of 0.1077 (as in [66]) with ϕ from 0.77 to 0.97 presented in Fig. 6. In both cases the new mechanism is in better agreement with experimental data in very lean hydrogen flames as compared to the Konnov [3] model, and closely approaches predictions of the ELTE [2] model.

Further reduction of the amount of oxygen in the oxidizer allows for covering a wider range of equivalence ratios as compared to H_2 + air flames due to experimental limitations discussed elsewhere [1]. Figure 7 shows the experimental data of Alekseev and

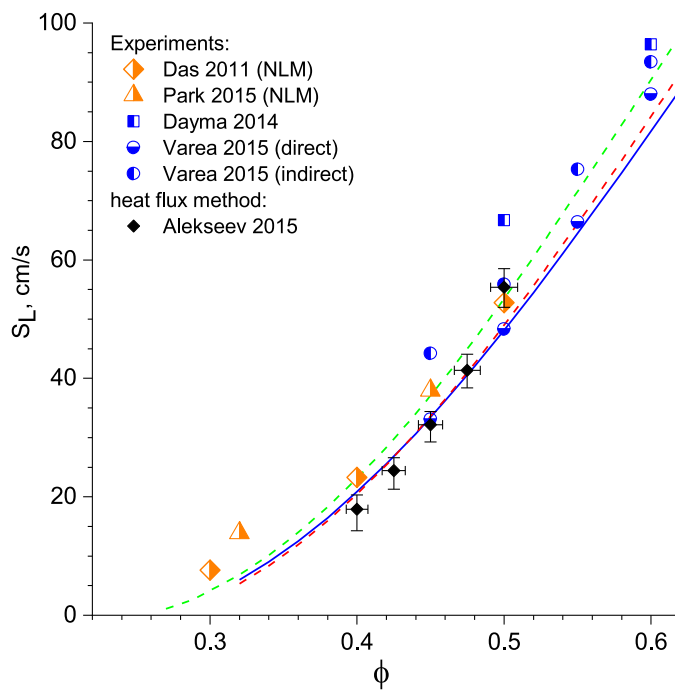


Fig. 5. Laminar burning velocity of lean H_2 + air flames at standard conditions. Symbols: experiments, black: Alekseev et al. [71], blue (spherical flame, NLM) – Dayma et al. [73], Varea et al. [72]; orange (counterflow, NLM) – Das et al. [74, 75], Park et al. [76]. Lines: calculations, green dashed line: Konnov [3], red dashed line: ELTE [2], solid blue line: present model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

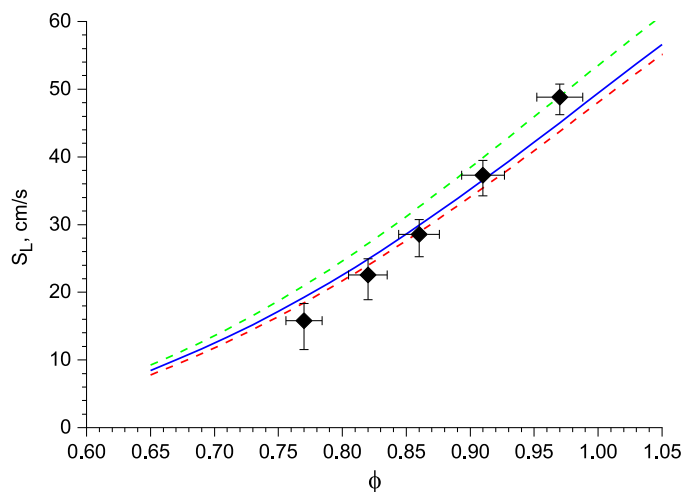


Fig. 6. Burning velocity of H_2 + O_2 + N_2 flames at atmospheric pressure and oxygen content in the oxidizer of 0.1077. Symbols: experiments [71]. Lines: calculations, green dashed line: Konnov [3], red dashed line: ELTE [2], solid blue line: present model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Konnov [1] for H_2 + O_2 + N_2 mixtures with the oxygen content of 0.077 (same as in Hermanns et al. [66]). Again, the new hydrogen kinetic mechanism accurately reproduces these measurements similar to the ELTE [2] model.

Voss et al. [69] used air as an oxidizer and dilute hydrogen in different proportions by N_2 to produce fuel mixtures with the amount of N_2 from 50 to 80%. Selected measurements at initial gas temperature of 298 K are presented in Fig. 8 together with similar study from the same group by Eckart et al. [70]. At these conditions the difference between predictions of the ELTE mechanism

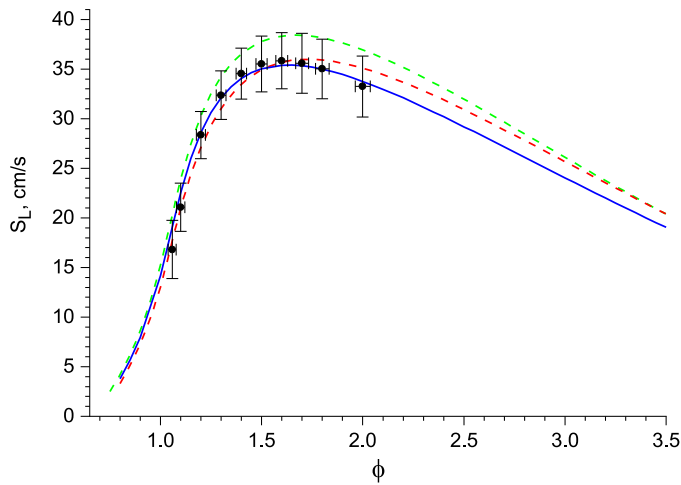


Fig. 7. Burning velocity of $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixture at atmospheric pressure with the oxygen content in the oxidizer of 0.077. Symbols: experiments [1]. Lines: calculations, green dashed line: Konnov [3], red dashed line: ELTE [2], solid blue line: present model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

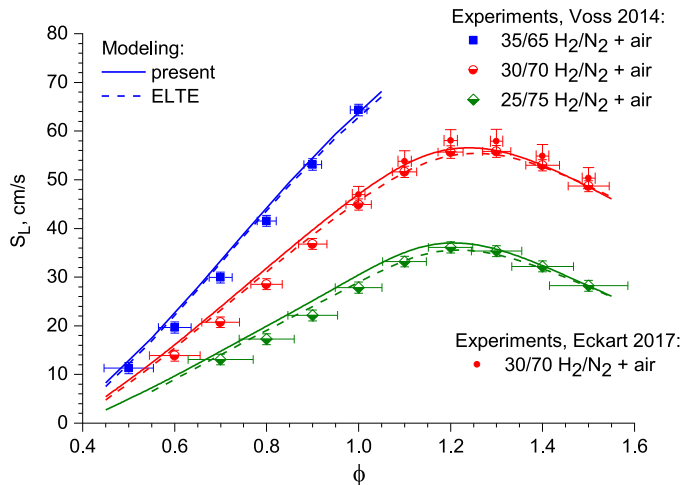


Fig. 8. Burning velocity of $(\text{H}_2 + \text{N}_2) + \text{air}$ flames at atmospheric pressure and temperature of 298 K. H_2 diluted by N_2 from 65 to 75%. Symbols: experiment [69, 70], lines: modeling. Dashed lines: ELTE [2], solid lines: present model.

[2] and the present model is very small and less than the typical experimental uncertainties.

In addition to revisiting some experiments of Voss et al. [69], Eckart et al. [70] also measured burning velocities at elevated initial temperature of 363 K for higher dilutions of H_2 by N_2 of 75 and 82%. Predictions of the both mechanisms compared in the present work are in better agreement with less diluted fuel mixture (Fig. 9).

Goswami et al. [65] investigated burning velocities of 85:15 ($\text{H}_2 + \text{N}_2$) mixture with 12.5:87.5 ($\text{O}_2 + \text{He}$) oxidizer from 1 to 10 atm at $\phi = 0.5$. These experiments were critically re-assessed by Alekseev and Konnov [1] performing new experiments at atmospheric pressure over the range of equivalence ratios 0.41–0.5 as shown in Fig. 10. It was concluded that due to malfunction of the equipment this original dataset of measurements [65] may have much higher experimental uncertainties and thus should not be used for model validation. The present mechanism is now in a good agreement with the experimental data contrary to the previous model [3].

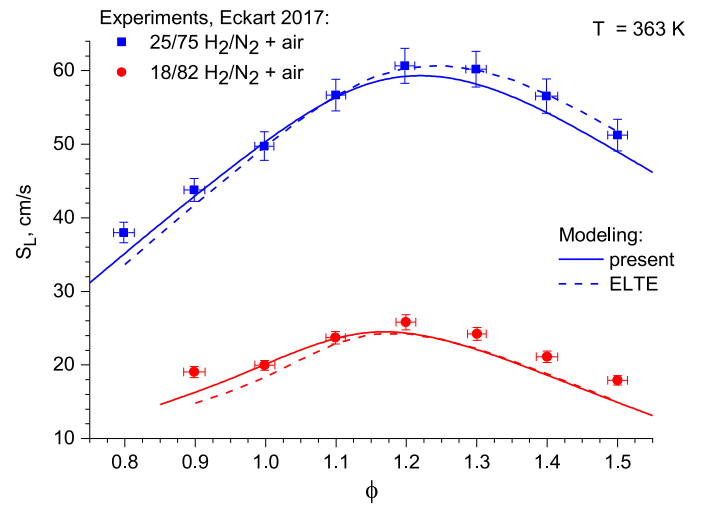


Fig. 9. Burning velocity of $(\text{H}_2 + \text{N}_2) + \text{air}$ flames at atmospheric pressure and temperature of 363 K. H_2 diluted by N_2 from 75 to 82%. Symbols: experiment [70], lines: modeling. Dashed lines: ELTE [2], solid lines: present model.

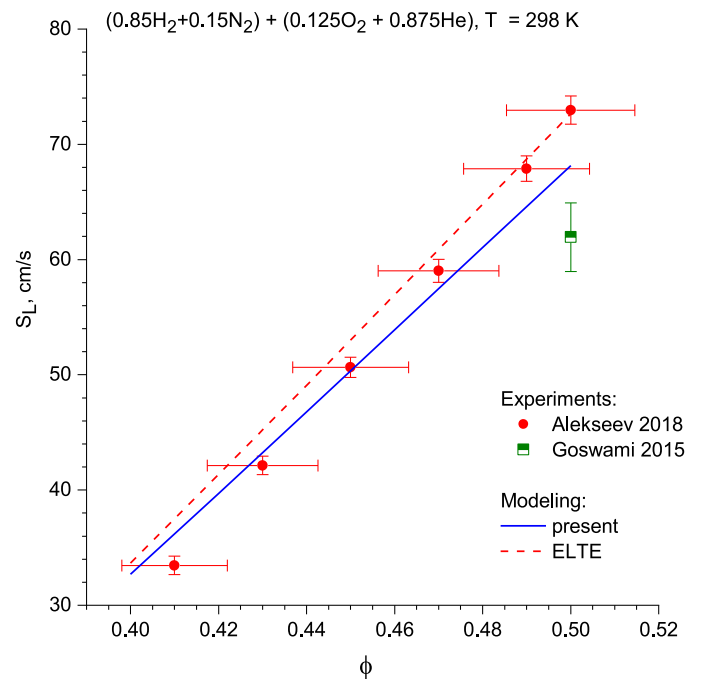


Fig. 10. Burning velocities of 85:15 ($\text{H}_2 + \text{N}_2$) mixture with 12.5:87.5 ($\text{O}_2 + \text{He}$) oxidizer at atmospheric pressure over equivalence ratios 0.41–0.5. Symbols: experiments, [1,65] lines: calculations. Dashed line: ELTE [2], solid line: present model.

The same oxidizer contained $\text{O}_2 + \text{He}$ in a proportion of 1:7 was used [1] to burn 25:75 ($\text{H}_2 + \text{N}_2$) fuel mixture from lean to rich flames. These measurements presented in Fig. 11 are nicely reproduced by both kinetic models. To illustrate once again the relative impact of the incorporation of chemically termolecular reactions and of the updated transport properties, predictions of the previous model [3], and of the model with all reactions from Table 1 included (keeping transport parameters the same as in [3]) are also shown in Fig. 11. Similar to hydrogen + air flames (Figs. 1 and S11) new reactions notably reduce calculated burning velocities mostly in stoichiometric and rich mixtures. Implementation of the new transport database leads to further decrease of the burning velocities in lean flames, while slightly increases them in rich flames. Summarizing overall performance of the previous model of the

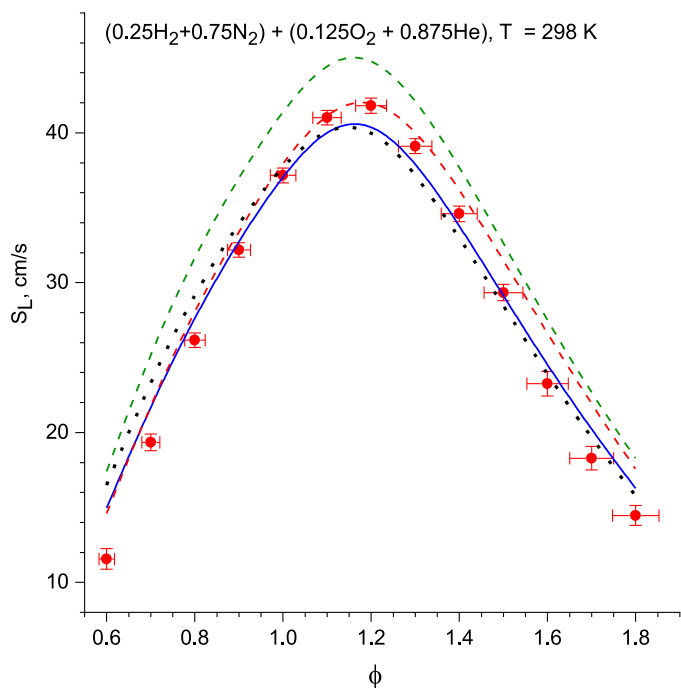


Fig. 11. Burning velocities of 25:75 ($\text{H}_2 + \text{N}_2$) mixture with 12.5:87.5 ($\text{O}_2 + \text{He}$) oxidizer at atmospheric pressure. Symbols: experiments [1], lines: calculations. Red dashed: ELTE [2], green dashed: Konnov [3], black dot line: all reactions included, solid blue line: present model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

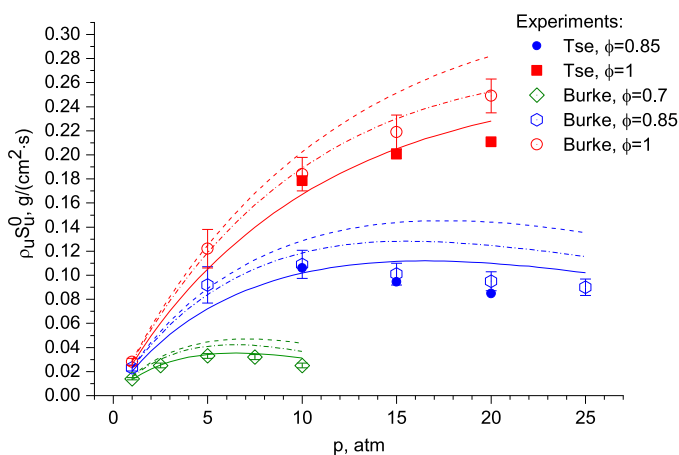


Fig. 12. Mass burning rate of $\text{H}_2 + \text{O}_2 + \text{He}$ mixtures at 295 K as a function of pressure at different equivalence ratios: $\phi = 0.7$ (green), $\phi = 0.85$ (blue), $\phi = 1$ (red). The O_2 content in the oxidizer is 8%. Experiments: [77, 78, 79]. Dashed lines: Alekseev et al. [16], dash-dot lines: Keromnes et al. [43], solid lines: present model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

author [3], the ELTE [2] mechanism and the present new model against consistent dataset of the burning velocity measurements using the heat flux method, one may conclude that updated kinetics and new transport properties implemented in the mechanism significantly improved its behavior, which is now close to, if not better than that of the optimized model.

All hydrogen flames presented so far were investigated at atmospheric pressure mostly at standard initial temperature of 298 K. It is therefore instructive to test the behaviour of the new kinetic mechanism at elevated conditions. Figure 12 shows mass burning rate of $\text{H}_2 + \text{O}_2 + \text{He}$ mixtures at 295 K from 1 to 25 atm. The experimental data are taken from Burke et al. [77,78]. The data at 298 K

from Tse et al. [79] are given for comparison. The new model is in much better agreement with these measurements compared to the model of Alekseev et al. [16] over entire range of pressures. Finally, the laminar burning velocity of $\text{H}_2 + \text{air}$ flames at atmospheric pressure at elevated initial temperatures of 373 and 443 K are presented in Fig. S12 in the Supplemental material. The measurements of Krejci et al. [9] are nicely reproduced by the new kinetic model similar to those at the standard conditions shown in Fig. 1.

6. Conclusions

The present study demonstrates that incorporation of the chemically termolecular reactions $\text{H} + \text{O}_2 + \text{R}$ 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.

Analysis of the recent experimental and theoretical kinetic studies of hydrogen reactions was also performed and three rate constants were updated. New expressions for the rate constants of reactions $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ [15,18] and $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ [26] are very close to the previously implemented as illustrated in Figs. 2 and 3, respectively. 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 [35], 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.

It was found that implementation of the new theoretical transport database developed by Jasper et al. [62,63] 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. At all experimental conditions previously scrutinized by Alekseev and Konnov [1] the new model closely approaches predictions of the ELTE [2] optimized mechanism.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2019.01.032.

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