

An Updated Comprehensive Kinetics Model of H₂ Combustion

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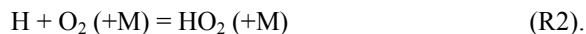
Introduction

The H₂/O₂ reaction mechanism plays a prominent role in fundamental chemical kinetics research as well as in the applied fields of fire safety, energy conversion and propulsion. The mechanism has been used extensively by several research groups including ours in various experiments to derive elementary reaction rate information, for example, by perturbations of kinetics using added species. Not only is hydrogen an important fuel for the above applications, but the elementary kinetics involving H, O, OH, HO₂, and H₂O₂ determine the composition of the radical pool in hydrocarbon reaction systems. The kinetics of the H₂/O₂ system and its behavior over a range of experiments conducted in a variable pressure flow reactor (VPFR) was recently discussed by Mueller et al [1]. The mechanism presented in [1] was extensively studied, but it was not tested against or modified as a result of experimental data derived in other types of experiments and in other parameter ranges. Indeed, the authors noted several issues that deserved further attention in applying the mechanism more generally. In the strictest sense, the published mechanism was therefore not “comprehensive”, a term originally applied by Westbrook and Dryer [2-4] to describe a mechanism developed by comparison against a number of different sources of kinetic data. These sources frequently include laminar flame speed measurements [5-8], shock tube ignition delay studies [9-13], and other sources such as static and stirred reactors. New flame speed experimental results using H₂/O₂/He mixtures at pressures ranging from 1 to 20atm appear to be poorly predicted by the Mueller et al mechanism [7], while predictions of similar experiments using H₂/O₂ mixtures in Argon, Helium and Nitrogen at 1 to 3atm pressure appear to be quite reasonable [8]. In recent unpublished work, Ó Conaire et al [14] have made wide-ranging comparisons with various experimental data and they have in addition noted that the mechanism in [1] substantially over predicts shock tube ignition delay data reported by Skinner et al [11].

Since publication of [1], there have been several important elementary kinetic publications further addressing two of the most important reactions involving the hydrogen radical, i.e., the branching reaction [15]



and the competitive reaction [16-18],



While some of the results presented in [18] were known at the time of our earlier consideration of (R2) [19], reference 18 contributes new insights to the magnitudes of and mechanism responsible for the apparent third body efficiencies of various species in (R2), particularly H₂O. In addition, the enthalpy of formation of OH has recently been conclusively revised [20].

In the present study, we update the mechanism of [1] based upon the new thermodynamic data and rate coefficients, and compare the updated mechanism against a wide array of experimental data including the original VPFR data, shock tube ignition delay data, and the new flame speed results to yield a “comprehensive” hydrogen oxygen mechanism.

We wish to emphasize, however, that the term “comprehensive” carries no inference as to whether a mechanism is “complete”, “unique”, and will never require further revisions. Additional experimental systems observations that increase the constraints which define the acceptability of predictive comparisons and/or improvements in uncertainties of elementary kinetic information (rate data, thermochemistry) can both inspire the need to revise a previously developed comprehensive mechanism. Thus, even “comprehensive” mechanisms should be reviewed in a timely manner as new information becomes available. This is a perplexing, but extremely important issue in light of the hierarchical nature of hydrocarbon kinetics and its dependence on H₂/O₂ kinetics. Revisions of mechanisms are likely to be necessary in perpetuity, given the nature of the field. Moreover, even the most complete mechanistic description to be envisioned will most likely never be “unique” in terms of the associated elementary reaction rate and thermochemical parameters.

Updated H₂/O₂ Chemical Kinetics

In the present work, the following parameters of mechanism presented in Mueller et al [1] were revised:

1. *The Enthalpy of Formation of OH.* Recently, Ruscic et al [20] studied the heat of formation of OH radical both experimentally and theoretically. Their recommended value of 8.85 kcal/mol at 0 K is used in the current mechanism.

2. *The Rate Constant of (R1).* We performed a sensitivity analysis of the original mechanism for a VPFR case at 3.4atm and 933K [1], for a premix laminar flame speed at 10atm [7], and for an ignition delay case under Skinner et al’s [11] shock tube condition. The normalized sensitivity coefficient of a reaction is defined as $\frac{\partial \ln Y}{\partial \ln k}$ and $\frac{\partial \ln s}{\partial \ln k}$ for the

disappearance of *Y* in a flow reactor and the laminar flame speed, respectively, where *k* is the rate constant, *Y* the mass fraction of a species (H₂ in this study), and *s* the laminar flame speed. The most sensitive reactions found are listed in Table 1 along with their sensitivity coefficients as defined above. The order of reaction sensitivities for the shock tube case is the same as that for the flow reactor.

Table 1. Sensitivity Coefficient of Reactions for a Flow Reactor and Laminar Flame Speed Case.

Reaction	Flow Reactor Case ^a	Laminar Flame Speed Case ^b
H + O ₂ = OH + O	-0.038	0.450
H + O ₂ (+M) = HO ₂ (+M)	0.040	-0.088
HO ₂ + H = OH + OH	-0.020	0.219
H ₂ + OH = H ₂ O + H	-0.006	0.204
HO ₂ + H = H ₂ + O ₂	0.012	-0.125
H ₂ + O = H + OH	-0.003	0.082
H + OH + M = H ₂ O + M	2.76E-5	-0.098

^a Initial condition: H₂ = 1.01%, O₂ = 0.52% with balanced N₂ at 3.4atm, 933K [1]. The sensitivity coefficient is calculated at when 50% H₂ disappears.

^b Initial condition: H₂ = 19.4%, O₂ = 6.5% with balanced He at 10atm, 298K [7].

The H₂/O₂ system is very sensitive to the key chain branching reaction (R1) and the important chain termination reaction (R2). Mueller et al [1] used the rate constant expression of Pirraglia et al [21] for the reaction (R1) and noted that while the expression over predicts the recent high temperature data above 1700K [22-24], it more properly predicts the rate at low temperatures. The recent analysis of Hessler et al [15] excluded consideration of certain sets of available elementary rate data [24] based upon a defined uncertainty envelope. The resulting rate constant correlation predicts not only the data in [21-23] but more closely predicts appropriate rates at low temperatures with in close proximity to those predicted by the expression in [21].

3. *The Low-pressure-limit Rate Constant of (R2).* The Troe formulation [25] is applied for reaction (R2) with the high-pressure-limit rate constant used in [1], and the low-pressure-limit results reported in [18]. Michael et al [18] measured and/or calculated the low-pressure rate constants with M = N₂, Ar, He, H₂, H₂O, and O₂. We fitted the data that were presented in the paper for each third body condition to capture both the rate constant and bath gas temperature dependences. The calculated fits in Arrhenius form for each specific bath gas are as follows (in units of cm⁶mol⁻²s⁻¹):

$$\begin{aligned}
 k_{N_2}^{R_2} &= 6.37 \times 10^{20} T^{-1.72} \exp(-264 / T) & k_{Ar}^{R_2} &= 9.04 \times 10^{19} T^{-1.50} \exp(-248 / T), \\
 k_{He}^{R_2} &= 7.65 \times 10^{19} T^{-1.45} \exp(-230 / T) & k_{H_2O}^{R_2} &= 1.65 \times 10^{22} T^{-1.83} \exp(-288 / T), \\
 k_{O_2}^{R_2} &= 3.19 \times 10^{20} T^{-1.52} \exp(-255 / T) & k_{O_2}^{R_2} &= 4.45 \times 10^{20} T^{-1.70} \exp(-260 / T).
 \end{aligned}$$

The fall-off range (R2) is described by taking the broadening factor F_c as 0.8 for N₂, 0.45 [1] for Ar, and 0.5 for He, H₂, H₂O, and O₂. Corresponding rates for other third bodies such as CO and CO₂ were calculated using the above low pressure rate constant with N₂ and the third body efficiencies of the species relative to N₂ reported in [1]. Figure 1 shows the branching ratio, i.e. (R2)/(R1), at 0.1, 1, and 10atm with the current revisions and from [1]. There is very good agreement (within 2%) at the conditions (800-900K) where the value of k_o used in [1] was experimentally derived [26]. At temperature higher than 2000K, the difference between the two predictions is larger (~30%), but (R2) is of no significance at these conditions relative to (R1).

4. *The Rate Constant of H + OH + M = H₂O + M, (R3).* The sensitivity analysis in Table 1 also illustrates that the laminar flame speed case is very sensitive to (R3), with the non-dimensional sensitivity increasing with pressure, while flow reactor and shock tube ignition delay predictions are essentially insensitive at all conditions to (R3). In order to improve flame predictions, we modified the A factor of the rate constant of (R3) to 3.8×10^{22} cm⁶mol⁻²s⁻¹ (from 2.2×10^{22} [1]). Ó Conaire et al [14] also suggest modification of this reaction to improve flame speed predictions. A review of the rate constants reported in the literature [27-32] for (R3) span more than an order of magnitude, with the value chosen here being in the middle of the range. Because of the large uncertainty in this rate constant, laminar flame speed predictions using any particular set of diffusion coefficients recommended by various authors can be forced to predict the same flame speed simply by adjusting the value of this single rate constant.

Results and Discussion

The mechanism updated as described above was compared against a wide range of experimental data, including laminar flame speed, shock tube ignition delay time, and the species profiles in the VPFR. The SENKIN code [33] was used to simulate experimental conditions in a shock tube and flow reactor. The PREMIX code [34] was used for laminar flame speed calculations. We used the standard CHEMKIN transport package with Soret effects and multi-component diffusion included. We imposed a minimum of 1000 grid points in the PREMIX calculation for a fully converged flame speed value. Representative test results are shown in Figures 2 – 8.

The comparison in Figures 2 and 3 shows that the predictions of the present mechanism are in excellent agreement with the laminar flame speed measurements for H₂/O₂/He mixture at pressures ranging from 1 to 20atm. The prediction of the laminar flame speed of H₂/O₂ system diluted by N₂ or Ar or He at 1atm is illustrated in Figure 4. Predictions also compare very well with shock tube ignition delay data, as is demonstrated with representative cases in Figures 5 – 6. Figures 7 and 8 compare predicted VPFR species profiles for H₂ oxidation at 3.4 and 0.3atm. Time-shift is used to compare the model predictions with the experimental measurement by shifting the simulated values along the time axis to match the 50% fuel consumption point. The validation against a wide range of experimental conditions discussed above demonstrates that the updated comprehensive mechanism does not require any complex optimization in order to reasonably predict a very wide range of experimental data. The updated mechanism in an electronic form compatible with Chemkin is available by e-mail request.

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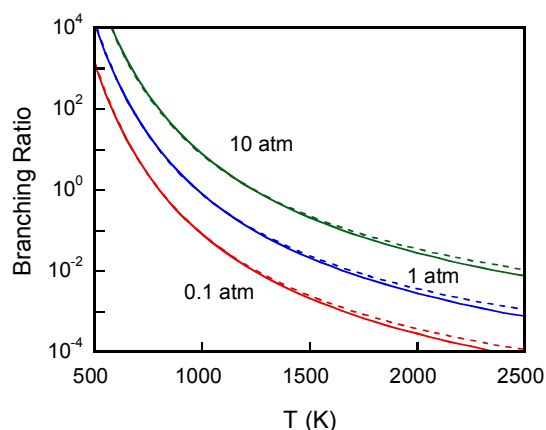


Figure 1. Branching ratio of the reaction (R1) and (R2). Solid line: present model; dashed line: Mueller et al [1].

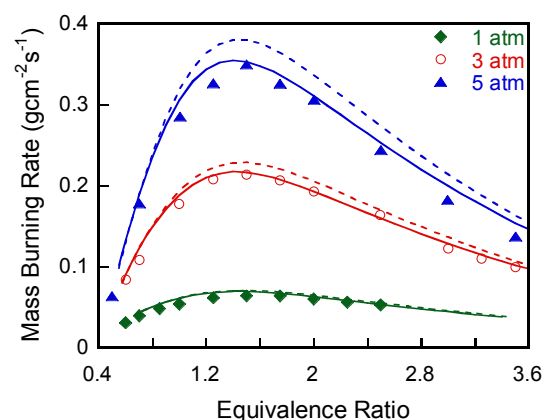


Figure 2. Laminar flame mass burning rate at 1, 3, 5atm for $\text{H}_2/\text{O}_2/\text{He}$ mixture ($\text{O}_2:\text{He} = 1:7$). Symbol: experimental data [7]; solid line: present model; dashed line: Mueller et al [1].

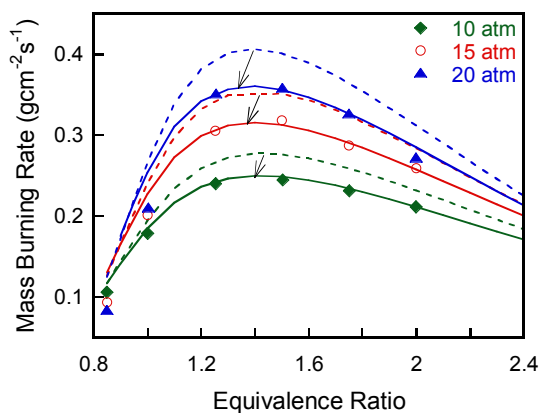


Figure 3. Laminar flame mass burning rate at 10, 15, 20atm for $\text{H}_2/\text{O}_2/\text{He}$ mixture ($\text{O}_2:\text{He} = 1:11.5$). Symbol: experimental data [7]; solid line: present model; dashed line: Mueller et al [1].

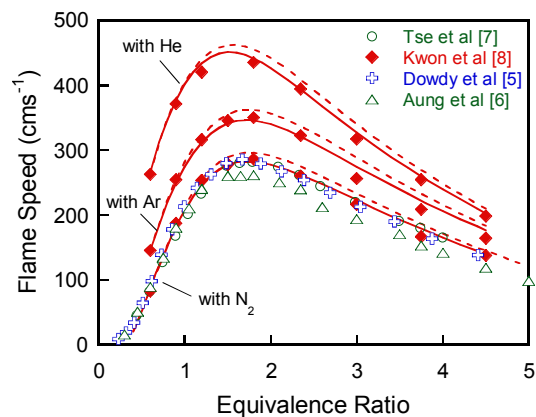


Figure 4. Laminar flame speed at 1atm for H_2/O_2 mixed with N_2 or Ar or He. ($\text{O}_2:\text{N}_2 = \text{O}_2:\text{Ar} = \text{O}_2:\text{He} = 1:3.76$). Symbol: experimental data [5-8]; solid line: present model; dashed line: Mueller et al [1].

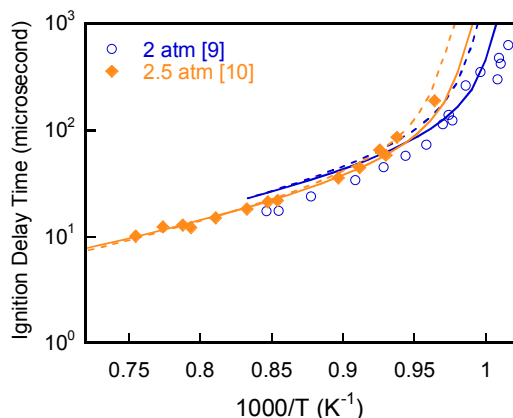


Figure 5. Ignition Delay time of $\text{H}_2/\text{O}_2/\text{N}_2$ mixture at 2atm or 2.5atm. ($\text{H}_2 = 29.6\%$, $\text{O}_2 = 14.8\%$, $\text{N}_2 = 55.6\%$). Symbol: experimental data [9,10]; solid line: present model; dashed line: Mueller et al [1].

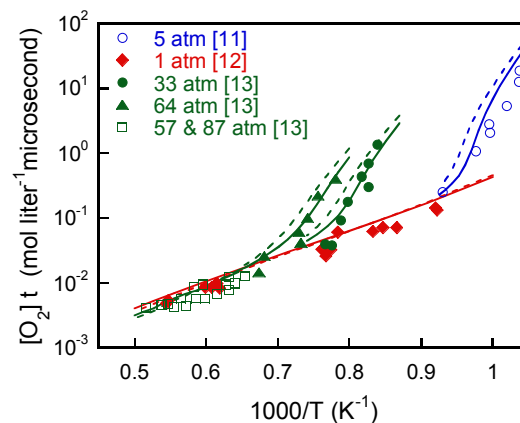


Figure 6. Induction times for $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures in shock tubes. Initial condition: $\text{H}_2 = 8.0\%$, $\text{O}_2 = 2.0\%$, $\text{Ar} = 90.0\%$ at 5atm [11]; $\text{H}_2 = 1.0\%$, $\text{O}_2 = 2.0\%$, $\text{Ar} = 97.0\%$ at 1atm [12]; $\text{H}_2 = 2.0\%$, $\text{O}_2 = 1.0\%$, $\text{Ar} = 97.0\%$ at 33, 57, 64, and 87atm [13]. Symbol: experimental data [11-13]; solid line: present model; dashed line: Mueller et al [1].

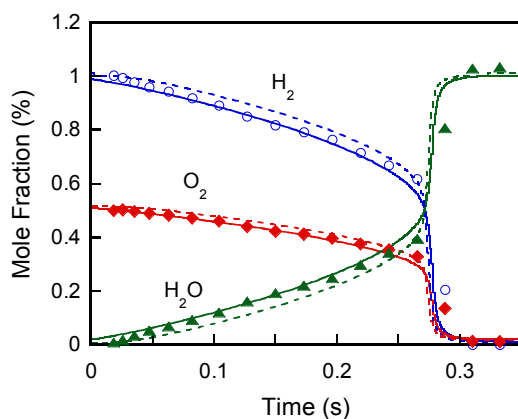


Figure 7. Reaction profiles of $\text{H}_2/\text{O}_2/\text{N}_2$ mixture in a flow reactor. Initial condition: $\text{H}_2 = 1.01\%$, $\text{O}_2 = 0.52\%$ with balanced N_2 at 3.4atm and 933K. Symbol: experimental data [1]; solid line: present model; dashed line: Mueller et al [1].

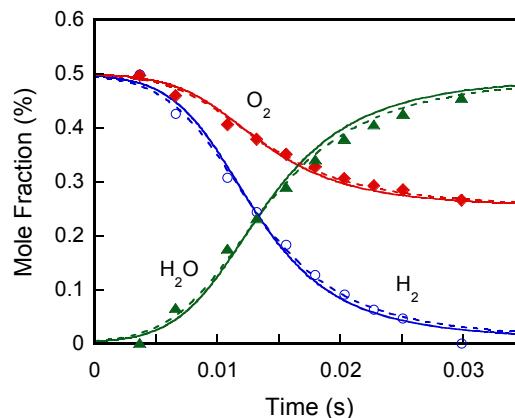


Figure 8. Reaction profiles of $\text{H}_2/\text{O}_2/\text{N}_2$ mixture in a flow reactor. Initial condition: $\text{H}_2 = 0.50\%$, $\text{O}_2 = 0.50\%$ with balanced N_2 at 0.3atm and 880K. Symbol: experimental data [1]; solid line: present model; dashed line: Mueller et al [1].