Laminar burning velocities of hydrogen-air flames with pressure variations

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1 Introduction

Description of hydrogen oxidation is important for at least two reasons: hydrogen is a renewable fuel, biologically or chemical derived, which burns intensely and cleanly and its oxidation mechanism forms the basic building block required in oxidation mechanisms of more complex molecules. Extensive research has been conducted experimentally [1-5] and numerically [6-11] on the reactivity of hydrogen/air or hydrogen/oxygen mixtures, included diluted mixtures and under high pressure conditions. Although the standard conditions are globally well simulated, pressure and equivalence ratio variations are less accurately captured [12]. Furthermore, whereas recent efforts concerned highpressure flames, only few recent data have been obtained under reduced pressure, where nonmonotonic variation of flame speed with pressure has been reported [13]. The sub-atmospheric conditions, and more specifically around 200 mbar, are of peculiar importance to guarantee a safe operation of an International Thermonuclear Experimental Reactor (ITER) [14]. Updates of hydrogen kinetic reaction mechanism have been recently presented by Hong et al [15], Burke et al. [12] and Keromnes et al. [16]. The model of Hong shows significant improvements regarding ignition delay prediction but brings no further resolution to discrepancies observed for flame speeds [15]. In the current study, the mechanisms of Burke et al. and Keromnes et al. were considered. Experimental measurements of laminar flame speed, analysis of the key reactions and kinetic pathways, and modeling studies were performed for H_2 -air premixed flames over a wide range of conditions: equivalence ratios from 0.5 to 4.0 and pressures from 0.2 to 3 bar. The experimental matrix was selected to check the validity of the two mechanisms over a wide range of pressures and equivalence ratios and to better understand the peculiar behavior of hydrogen flame speeds according to the pressure.

2 Experimental set-up

The laminar flame burning velocity measurements were performed using a stainless steel spherical combustion chamber with an inside volume of 4.2 L used previously [17]. Four windows provided optical accesses into the chamber. Before filling, a vacuum was created inside the chamber. The volumes of air (Synthetic air : 79.1% N₂ and 20.9% O₂) and hydrogen were introduced into the chamber with a thermal mass flow controller. The temperature of the chamber was regulated at a

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desired value of $T_u = 303$ K. Inside the chamber, an electric fan mixed the reactants. Ignition was delayed to avoid any perturbation during the flame propagation experiments. Two tungsten electrodes separated by 1 mm, connected to a capacitive discharge ignition system, were used for spark ignition at the chamber center. Measurements were limited to flames with diameters < 50 mm, which corresponds to a total volume of burned gases < 1.6% of the volume of the chamber. Through the initial stage of the flame expansion, the inside chamber total pressure can be considered constant. For each condition, the measurements were repeated three times. The standard deviation corresponding to the scattering in experiments $(\pm 2 \text{ cm/s})$ is contained in the symbol size. Shadowgraphy was used to record flame images. Parallel light was obtained from an Ar-Ion laser source with two plano-convex lenses of respectively 25 and 1000 mm focal lengths. The shadowgraphic images recorded using a high speed video CMOS camera (Photron APX) operating at 20000 frames per second with an exposure time of 20 µs were used to analyze the temporal evolution of the expanding spherical flames. After the spark, the flame front propagates spherically and the temporal flame radius evolution is postprocessed using a non-linear relation between the flame propagation speed and the stretch as described in [18]. Finally, the laminar speed is evaluated from the propagation speed using the expansion ratio. The densities of the burned gases were evaluated using the chemical composition at the constant pressure adiabatic conditions.

3 Computational methods

Two very recent and extensively validated kinetic mechanisms were selected to model our experimental results. The first mechanism by Burke et al. [12] is an updated version of that by Li et al. [6]. This chemical kinetic mechanism consists of 19 reactions involving 9 species and was specifically developed for high pressure purpose. The second mechanism by Keromnes et al. [16] is an updated version of the mechanism presented earlier [10]. This chemical kinetic mechanism also consists of 19 reactions and 9 species. It has been extensively validated over a large number of experimental conditions. Both of these mechanisms were used with their own thermodynamic and transport data.

Computations were performed using the CHEMKIN package and the PREMIX code [19]. All the laminar burning velocities were calculated with the same conditions of gradient and curvature (GRAD = 0.01 and CURV = 0.01) leading to a similar number of meshes for each equivalence ratio or pressure of around 1000. These conditions allow the calculated laminar burning velocity to vary by less than 2.5% between the two last calculation steps.

4 Results

The first step consisted in comparing experimental and numerical results at ambient conditions (P = 1 bar - $T_u = 303$ K) and for equivalence ratios ranging from 0.5 to 4.0 (Figure 1). As can be seen from Fig. 1, an excellent agreement was observed with our experimental data over the entire equivalence ratio range. The laminar burning velocity steeply increases from $\phi = 0.5$ to 1.7 and then slowly decreases from $\phi = 1.8$ to 4. As well, despite the differences between the two mechanisms, they both predict very similar laminar burning velocities over the present range of experimental conditions.

We also compared our experimental results obtained at four different equivalence ratios (0.5, 1, 1.7, and 3) as a function of pressure to the laminar burning velocities calculated with both of these kinetic mechanisms. This comparison is plotted in Figure 2 together with data from the literature. Again, the agreement between our data and the calculations is very satisfactory, although a slight discrepancy (< 15%) is observed at very low pressures (< 0.7 bar). Our experimental data are also in very good agreement with data from the literature. According to our experimental results, at $\varphi = 0.5$, hydrogen flame speeds decrease with total pressure from 0.2 to 2 bar, whereas at $\varphi = 1.7$, the flame speeds increase from 0.3 to 1.7 bar and at $\varphi = 3$, flame speeds first increase with the pressure, reach a maximum around P = 1.2 bar and then decrease while total pressure increases. These results seem to

indicate that the pressure for which the flame speed reaches a maximum depends on the equivalence ratio.



Figure 1. Laminar burning velocity of hydrogen/air mixtures at ambient conditions (P = 1 bar and $T_u = 303$ K). Open diamonds represent the present experimental results, while full line and dashed line represent the computed results with Keromnes' and Burke's mechanisms respectively.

To determine these pressures, we performed step by step calculations with the Keromnes mechanism [16] and reported, for each equivalence ratio, the pressure for which the flame speed reaches a maximum. These P_{max} are represented in Figure 3. P_{max} first increases with the equivalence ratio from 0.1 bar at $\varphi = 0.5$ to 2.15 bar at $\varphi = 1.7$, then P_{max} decreases down to 0.3 bar at $\varphi = 5.9$. To explain this dependence on the equivalence ratio, reaction pathways analyses were performed using the Keromnes mechanism [16] for five equivalence ratios (0.5, 1.0, 1.7, 3.0, and 5.0) as a function of pressure at T = 1100 K. For each analysis, the rates of the reaction $H + O_2 = OH + O$ and the reaction $H + O_2 + M =$ $HO_2 + M$ were reported. $H + O_2 = OH + O$ is the main branching step, responsible for the system reactivity to increase. Hence, this reaction was expected to be dominant when the flame speed increases with pressure. $H + O_2 + M = HO_2 + M$ is the pressure-dependent competing termination step, reducing the system reactivity. Hence, this reaction was expected to be dominant for pressures higher than P_{max}, when the flame speed decreases with increasing pressure. Then, for each equivalence ratio, we plotted the ratio between the rates of the branching and the termination reaction versus pressure and determined under which pressure both of these rates were equal, i.e., at which pressure H-atoms were equally consumed by $H + O_2 = OH + O$ than by $H + O_2 + M = HO_2 + M$. This competition between the temperature-sensitive two-body branching reaction and the temperature-insensitive threebody chain termination reaction, suspected to be responsible for the equivalence ratio dependence of P_{max} [20] is represented as black crosses in Fig. 3. Indeed, it appears that this competition cannot solely explain the equivalence ratio dependence of P_{max} . At $\phi = 0.5$, if the flame speed were only dependent on this competition, it would increase until the pressure reaches 0.7 bar. Above this pressure, the flame speed would decrease, i.e. P_{max} would be 0.7 bar instead of 0.1 bar. At $\phi = 1.7$, the only competition would have made $P_{max} = 1.3$ bar whereas the pressure for which the laminar burning velocity reaches a maximum is 2.15 bar. Considering the only competition between the branching and termination steps makes P_{max} converge to 1.4 bar when the equivalence ratio increases further, which is not what we observed.



Figure 2. Laminar burning velocity of hydrogen/air mixtures according to the initial pressure at $T_u = 303$ K and (a) $\phi = 0.5$, (b) $\phi = 1.0$, (c) $\phi = 1.7$, and (d) $\phi = 3.0$. Symbols are experimental results, lines are calculations.

Considering additional phenomena is required to explain the peculiar variation of hydrogen laminar burning velocity as a function of total pressure and equivalence ratio. At $\varphi = 5$ for instance, other pathways consume H atoms such as $H + H + M = H_2 + M$ at low pressure and $H + HO_2 = OH + OH$ when the pressure increases. Diffusion was also found to be a sensitive parameter: dividing the collision diameter of N₂ by factor 2 results in a shift towards higher pressures of P_{max} at $\varphi = 0.5$ or $\varphi = 1.7$. This modification also increases the flame speed for both equivalence ratios, however, at $\varphi = 0.5$ the increase is calculated to be between 44% at P = 0.05 bar and 114% at P = 4 bar, whereas at $\varphi = 1.7$, the increase is very similar all over the pressure range, from 22% at P = 0.05 bar to 30% at P = 5 bar, indicating diffusion is mostly sensitive at low equivalence ratios.



Figure 3. Pressure at which the maximum laminar burning velocity of hydrogen/air mixtures at $T_u = 303$ K (P_{max}) occurs as a function of equivalence ratio. Diamonds were calculated using the Keromnes mechanism [16], crosses were calculated only taking into account the competition between H+O₂=OH+O and H+O₂+M=HO₂+M (see text).

Conclusion

The present paper experimentally and numerically investigated the reactivity of hydrogen/air mixtures under both sub- and supra-atmospheric pressure conditions. Two recent mechanisms were selected for the interpretation of the experiments. Comparisons were performed over a wide range of conditions: equivalence ratio varied from 0.5 to 4.0 and pressure ranged from 0.2 to 3 bar. An excellent agreement was observed between the modeling and experimental results, confirming the validity of the kinetic schemes selected. A non-monotonic variation of hydrogen/air flame speed with pressure was observed and several explanations were proposed. The non-monotonic evolution is partly due to the competition between the temperature-sensitive two-body branching reaction, $H + O_2 = OH + O$, and the temperature-insensitive three-body chain termination reaction $H + O_2 + M = HO_2 + M$. Additional pathways consuming H atoms (i.e., $H + H + M = H_2 + M$ and $H + HO_2 = OH + OH$) and diffusion were also identified as sensitive parameters.

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