Laminar Burning Velocities of Diluted Hydrogen−Oxygen−Nitrogen Mixtures

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Measurements of laminar adiabatic burning velocities of flames propagating in hydrogen−oxygen−nitrogen mixtures at atmospheric pressure are presented and analyzed in this study. The oxygen content in the oxidizer (nitrogen−oxygen mixture) was varied between 0.07 and 0.1 (7−10 volume percent) at an equivalence ratio of 1.058. Besides the variation in oxygen content a variation in equivalence ratio from 0.7 to 3.1 and from 0.7 to 0.95 is presented at oxygen contents of 0.077 and 0.1077, respectively. The heat flux method was used to determine burning velocities under conditions where the net heat loss of the flat stretchless flame to the burner is zero. The resulting adiabatic burning velocities are presented with error margins using a 95% confidence interval. A significant difference was found when comparing the present results with experimental data from the literature.

Introduction

The burning velocity is an important characteristic needed for the understanding of combustion processes. Moreover, it is one of the key parameters which governs the stabilization of flames on burners and has for instance a direct important influence on the limits of flash-back and lift-off of the flame. Furthermore, on a fundamental level the burning velocity contains information of reactive and diffusive properties of a mixture. Finally, experimental measurements of laminar burning velocities are of key importance for validation of detailed reaction mechanisms.

Burning velocities of hydrogen−air mixtures as a function of temperature, pressure, and stoichiometric ratio have been measured by many investigators; however, the data were inconsistent for a long time. For instance, the earlier measurements summarized in 1983 by Liu and MacFarlane[1] possess a spread of the maximum burning velocity at atmospheric pressure and room temperature from about 260 to 350 cm/s. Wu and Law[2] demonstrated experimentally that the flame stretch due to flame front curvature and/or flow divergence must be taken into account in the data processing. The methodology of the determination of laminar burning velocity with the counterflow twin-flame technique by extrapolation to zero stretch rate has been further improved by Vagelopoulos et al.[3] In constant volume bombs, the unstretched burning velocities of hydrogen−air mixtures were determined subsequently by Dowdy et al.,[4] Karpov et al.,[5] Aung et al.,[6,7] Tse et al.,[8] Kwon and Faeth,[9] and Lamoureux et al.[10] using essentially the same approach.

Figure 1 shows measured laminar burning velocities of hydrogen−air flames at standard initial temperature (298 K) and atmospheric pressure as a function of the hydrogen mole fraction in the mixture. The measurements generally agree within experimental uncertainties, while those of Aung et al.[6,7] are somewhat lower than others in rich flames. The experimental uncertainty of the laminar burning velocities derived from expanding spherical flames was estimated by Aung et al.[6] and by Kwon and Faeth[9] to be about 10%.

Continuous experimental efforts[1−10] enable one to conclude that laminar burning velocities of hydrogen−air flames are consistent and measured with satisfactory accuracy. However, the available reliable data for the burning velocities of hydrogen−oxygen−nitrogen mixtures with oxidizer composition different from that of air are very scarce. In the development of detailed, comprehensive chemical mechanisms for the modeling of combustion phenomena, model validation through comparison with reliable experimental data is very important. Diluted mixtures of hydrogen burn at much lower temperatures as compared to hydrogen + air flames. Therefore, measurements of laminar burning velocities in diluted flames extend the basis for the model validation toward lower temperatures. Diluted $H_2−O_2−N_2$ flames were studied using the counterflow twin-

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(3) Vagelopoulos, C. M.; Egolfopoulos, F. N.; Law, C. K. *Proceedings of the Twenty-fifth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1994; pp 1341−1347.
(4) Dowdy, D. R.; Smith, D. B.; Taylor, S. C.; Williams, A. *Proc. Combust. Inst.* **1990,** *23*, 325−332.

(5) Karpov, V. P.; Lipatnikov, A. N.; Wolanski, P. *Combust. Flame* **1997**, *109*, 436−448.
(6) Aung, K.T.; Hassan, M. I.; Faeth, G.M. *Combust. Flame* **1997**, *109*, 1−24.
(7) Aung, K.T.; Hassan, M. I.; Faeth, G. M. *Combust. Flame* **1998**, *112*, 1−15.
(8) Tse, S. D.; Zhu, D. L.; Law C. K. *Proc. Combust. Inst.* **2000**, *28*, 1793−1799.
(9) Kwon, O. C.; Faeth, G. M. *Combust. Flame* **2001**, *124*, 590−610.
(10) Lamoureux, N.; Djebaili-Chaumeix, N.; Paillard, C.-E. *Exp. Therm. Fluid Sci.* **2003**, *27*, 385−393.
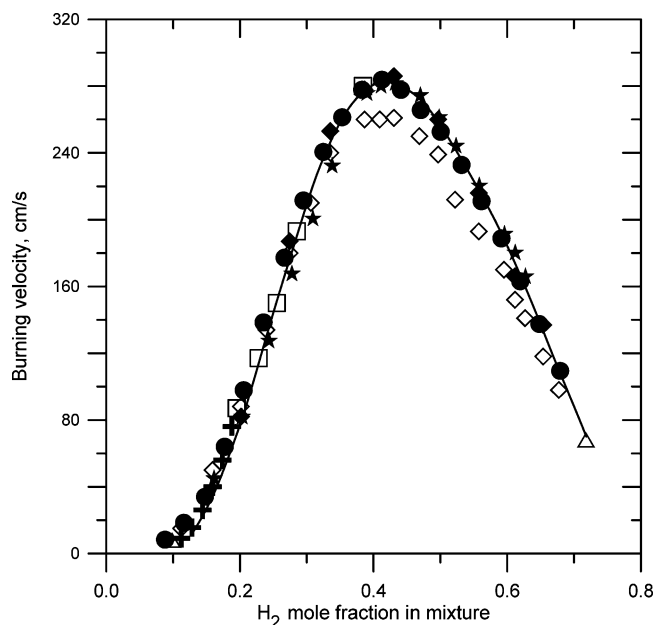
Figure 1. Measured (points) and calculated with the mechanism described in the modeling section (line) unstretched laminar burning velocities for hydrogen−air flames at standard temperature and pressure. Squares, Wu and Law;[2] crosses, Vagelopoulos et al.;[3] circles, Dowdy et al.;[4] triangles, Karpov et al.;[5] open diamonds, Aung et al.;[6,7] stars, Tse et al.;[8] and solid diamonds, Kwon and Faeth.[9]

flame technique.[11] The accuracy of this technique is limited by the accuracy of the laser doppler velocimetry (LDV), which was estimated to be 1−2 cm/s for burning velocities less than 60 cm/s and up to 10 cm/s for those above 170 cm/s.[11] Additional significant uncertainty of the counterflow method is due to the linear extrapolation to zero stretch rate. This has been recognized and demonstrated by Vagelopoulos et al.[3] for hydrogen−air flames. They showed that nonlinear correction was more accurate. An increasing difference between corrected and non-corrected laminar burning velocities toward lean, slowly burning hydrogen−air mixtures was found.[3] Regrettably, the results obtained for $H_2-O_2-N_2$ mixtures with varying oxygen content[11] have not been corrected for these effects.

For these reasons, the propagation of adiabatic laminar premixed flames in mixtures of $H_2-O_2-N_2$ has been studied experimentally in the present work. For performing accurate measurements of the adiabatic burning velocity, the heat flux method has been used, which was developed at the Eindhoven University of Technology in the past decade.[12,13] This method has been proven to be accurate with typical experimental uncertainty of 1 cm/s and below.[12] To find the adiabatic burning velocity with the heat flux method there is no need to extrapolate experimental results. In fact the adiabatic burning velocity is found by interpolation, because flames for which the unburnt gas velocity is slightly higher or lower (typically a few cm/s) than the adiabatic burning velocity still remain flat and can stabilize on the burner.

In the following sections, the experimental method is shortly outlined together with an analysis of the expected error margins. The numerical method is shortly specified afterward. Finally

the measurement results and error margins with a 95% confidence interval are presented for the burning velocity (S_L) of flames in hydrogen−oxygen−nitrogen mixtures. The oxygen content in the oxidizer, $O_2/(O_2 + N_2)$, was varied between 0.07 and 0.1077. The fuel equivalence ratio (φ) was varied between 0.7 and 3.1. The results are compared with other experimental data from the literature and numerical results using a detailed chemical kinetics mechanism.

Experimental Section

Detailed descriptions of the heat flux method and experimental setup can be found elsewhere.[12,13] Only the most essential characteristics are described in this paper. Figure 2 shows the schematic of the burner. It consists of a plenum chamber and a burner head. The outlet of the burner head consists of a plate perforated with small holes. Eight thermocouples were soldered to the plate surface at the upstream side. The burner head has a heating jacket with thermostatic water supply kept at 360 K in the present experiments. The plenum chamber has an independent thermostatic jacket, and its temperature was kept at 298 K. Thus, during the measurements the burner plate's temperature was higher than the initial gas temperature, and the unburned gases passing through it were heated.

The distance between the flame front and the burner (and therefore heat losses) depends on the imposed flow rate. When the flame was stabilized under sub-adiabatic conditions, the gas velocity was lower than the adiabatic flame burning velocity. The heat gain of the burner plate exceeded the heat loss. In this case the center of the burner plate was hotter than the heating jacket. If the unburned gas velocity was higher than the adiabatic burning velocity (super-adiabatic conditions), the net heat flux was lower than zero and the center of the burner plate was cooler than the heating jacket. By changing the flow rate of the gas mixture an appropriate value of the gas velocity can be found to nullify the net heat flux. In this case the radial temperature distribution in the burner plate becomes uniform and equal to the temperature of the heating jacket. The flow rate at which the net heat flux is zero has been shown to be equal to the adiabatic flame burning velocity.[13,14]

The gas supply system consists of three channels for the hydrogen, oxygen, and nitrogen. Each channel is connected to an appropriate gas cylinder and has a buffer vessel and a mass flow controller (MFC). Two water thermostats are used to provide the water supply to the thermostatic jackets of the burner.

Bosschaart and de Goey[12] introduced a thorough analysis of the heat flux method to measure the adiabatic burning velocity S_L. The first contribution to the error estimation for φ and S_L was derived from the uncertainties of the MFCs. The relative error of the MFCs increases when producing smaller flows. Therefore it is important to choose appropriate dimensions for the MFCs to keep the error in φ small. The error estimate in the equivalence ratio has a typical value of ±0.03 with a 95% confidence interval. The second contribution to the error in the burning velocity can be attributed to the scatter in the temperatures found by the thermocouples at different radii. This effect was also taken into account.[12] This error mostly depends on the heat release of the flame and increases toward very lean and very rich mixtures. Typical values of the error in the burning velocity fall within an absolute value of 1 cm/s. However, in slowly burning flames, both errors for φ and S_L, as estimated in the present work, increase. This will be discussed in the following.

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(12) Bosschaart, K. J.; de Goey, L.P.H. *Combust. Flame* **2003**, *132*, 170−180.

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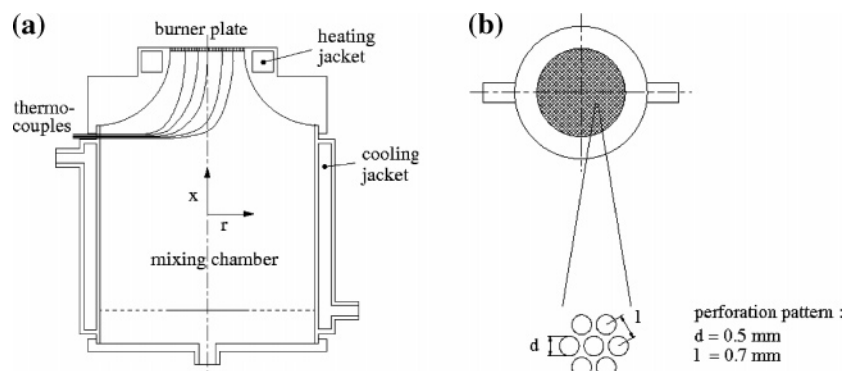
Figure 2. Schematic of the heat flux burner. (a) The heat flux burner. (b) Top view of the burner showing the perforation pattern of the burner plate.

Modeling Details

The Chemkin Collection of Codes Release 3.6[15] is used for the flame modeling. Multicomponent diffusion and thermal diffusion options are taken into account. Adaptive mesh parameters are GRAD = 0.02 and CURV = 0.5, and additionally the central differencing formulation is used for the convective terms. Transport properties are used taken from Sandia National Laboratories.[15] The calculations are performed with an unburnt mixture temperature of 298 K at atmospheric pressure. The current version of the hydrogen combustion scheme used in the present study is largely based on the recently developed mechanism by Konnov.[16] The reaction mechanism, including thermochemistry data, is available as Supporting Information (in Chemkin format). The purpose of the calculations is to ensure that this mechanism is suitable for numerical modeling of diluted flames of hydrogen. Results with the mechanism demonstrated very good performance in predicting laminar burning velocities of hydrogen−air flames (Figure 1). Thus the mechanism can be assessed more severely with respect to its predictive capabilities for the current conditions.

Results and Discussion

The experimental results for the laminar burning velocity (S_L) are presented in Figures 3−5. The measurements and modeling are performed with a gas flow temperature of 298 K and ambient pressure. The results are compared with the experimental data of Egolfopoulos and Law[11] and numerical simulations. In Figure 3 the results with varying oxygen content in the oxidizer $O_2/(O_2 + N_2)$ and constant $\varphi = 1.058$ are presented with 95% confidence interval error bars. These error bars for the oxygen fraction and for the burning velocity are derived using the procedure developed by Bosschaart and de Goey.[12] The error estimate for the oxygen fraction varies between 0.0013 and 0.0017. The largest error occurs at highly diluted mixtures by nitrogen, $O_2/(O_2 + N_2) \approx 0.07$, due to the fact that the MFCs have been used in very low working range as the mass flows rates are low in this region. The error estimate for the laminar burning velocity varies between 0.34 and 0.76 cm/s. An additional reason for the relative large errors is because of the low heat release of the flame in these mixtures.

When comparing the experimental results of Egolfopoulos and Law[11] with those of the heat flux method, the latter show
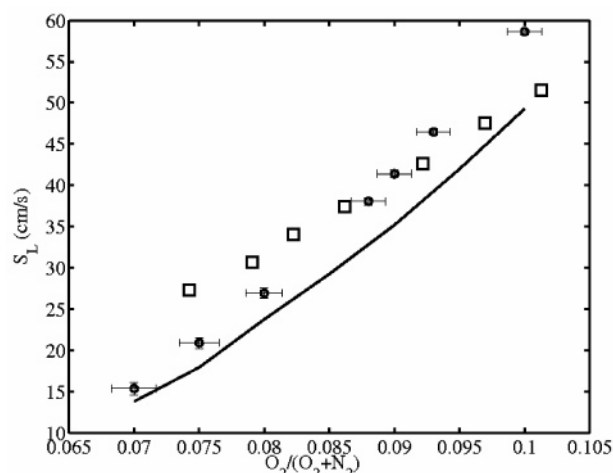
(15) Kee, R. J.; Rupley, F. M.; Miller, J. A.; Coltrin, M. E.; Grcar, J. F.; Meeks, E.; Moffat, H. K.; Lutz, A. E.; Dixon-Lewis, G.; Smooke, M. D.; Warnatz, J.; Evans, G. H.; Larson, R. S.; Mitchell, R. E.; Petzold, L. R.; Reynolds, W. C.; Caracotsios, M.; Stewart, W.E.; Glarborg, P.; Wang, C.; Adigun, O. *Chemkin Collection*, Release 3.6; Reaction Design, Inc.: San Diego, CA, 2000.
(16) Konnov, A. A. *Khim. Fiz.* **2004**, *23* (8), 5−28.

Figure 3. Laminar burning velocities of H₂−O₂−N₂ mixtures at an equivalence ratio of 1.058 with different oxygen fractions in the oxidizer stream. The measurements and modeling were performed with a gas flow temperature of 298 K and ambient pressure. Circles, heat flux measurements; squares, measurements by Egolfopoulos and Law;[11] and line, calculations.
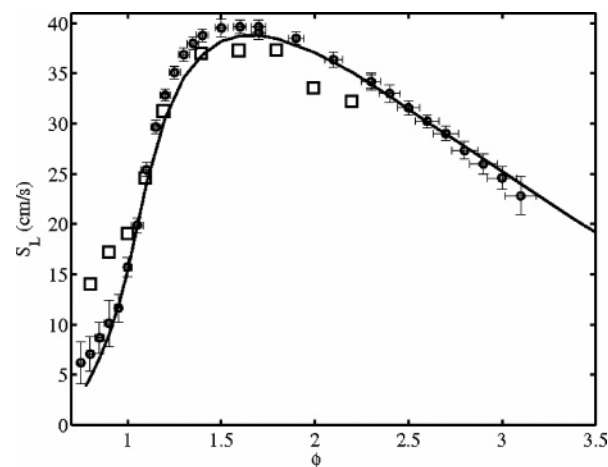

Figure 4. Laminar burning velocities of H₂−O₂−N₂ mixtures at O₂/(O₂ + N₂) = 0.077 with different equivalence ratios. The measurements and modeling were performed with a gas flow temperature of 298 K and ambient pressure. Circles, heat flux measurements; squares, measurements by Egolfopoulos and Law;[11] and line, calculations.

lower laminar burning velocities for an oxygen fraction up to 0.09, whereas above an oxygen content of 0.09 their results are lower than the heat flux measurements. The largest difference between the experimental results in the present range of measurements is found around an oxygen content of 0.075 and
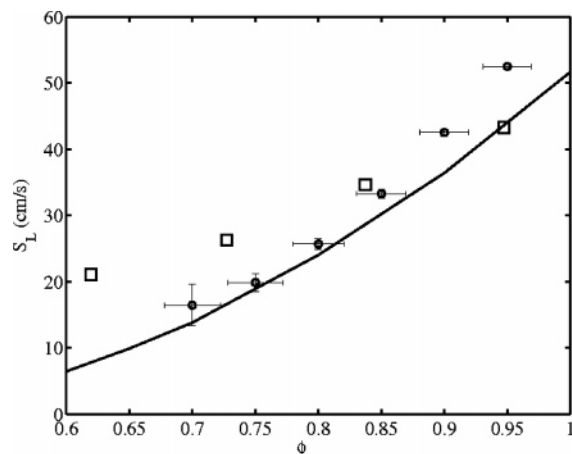
Figure 5. Laminar burning velocities of $H_2-O_2-N_2$ mixtures at $O_2/(O_2 + N_2) = 0.1077$ with different equivalence ratios. The measurements and modeling were performed with a gas flow temperature of 298 K and at ambient pressure. Circles. heat flux measurements; squares, measurements by Egolfopoulos and Law;[11] line, calculations.

0.1 where it is approximately 6 cm/s because of different apparent slopes (Figure 3). It should be emphasized that the discrepancy between the measurements of Egolfopoulos and Law and the heat flux method is outside the presented experimental errors. The authors[11] assumed that the uncertainty of the counterflow twin-flame technique was limited by the accuracy of the LDV method, which was estimated to be 1–2 cm/s for burning velocities less than 60 cm/s. Significant possible uncertainty of the method of linear extrapolation to zero stretch rate has been recognized and demonstrated later for hydrogen–air flames.[3] The difference between linear correction and nonlinear correction increases toward lean, slowly burning mixtures.

Measurements of laminar burning velocities with varying equivalence ratio and constant dilution ratio of $O_2/(O_2 + N_2)$ = 0.077 and 0.1077 are presented in Figures 4 and 5, respectively. In Figure 4, uncertainty of φ, as determined with the heat flux method, ranges from 0.017 to 0.085. The maximum value is around $\varphi = 3.1$, and the minimum value occurs at $\varphi = 0.8$. For the uncertainty of the burning velocity the values vary between 0.57 and 2.3 cm/s. Here the maximum occurs at $\varphi = 0.9$ whereas the minimum value occurs at $\varphi = 1.2$. Similar to the case of variation of nitrogen dilution, the low heat release of these flames increases the error in the laminar burning velocity. Between $\varphi = 1.2$ and 1.8 the flame exposes the highest heat release, which has a positive effect on the error of the laminar burning velocity. When the equivalence ratio is further increasing, the error increases again due to a lower heat release of the flames. A similar conclusion can be drawn from Figure 5, where the uncertainty of φ ranges from 0.019 to 0.022 and the uncertainty of S_L is between 0.4 and 3.1 cm/s. The last value, which can be defined as the limiting point of the measurements, significantly exceeds the typical uncertainty of the heat flux method mentioned above (1 cm/s). This is due to the fact that the relative error of the MFCs increases when producing smaller flows of hydrogen in very lean flames and of oxygen in very rich ones.

The experimental results of Egolfopoulos and Law[11] are also shown in Figures 4 and 5. Generally, one may conclude that the heat flux method gives lower laminar burning velocities compared to the measurements of Egolfopoulos and Law. However, a higher burning velocity is found with the heat flux method for a dilution ratio of 0.1077 and equivalence ratio of 0.95, compared to the counterflow flame at that point. Near φ

= 0.7 the difference in laminar burning velocity is about 10 cm/s. It is interesting to note that the deviation with the measurements obtained by the counterflow twin-flame technique[11] and compared with the results using the heat flux method in non-stretched flames changes its sign at an equivalence ratio around 0.9. Davis and Searby[17] demonstrated recently that the Markstein number in hydrogen–air flames also changes sign in these slightly lean mixtures. One might expect therefore that the linear extrapolation to zero stretch rate[11] might be an important reason for the discrepancy between the experimental results shown in Figures 3–5.

Also shown in Figures 3–5 are the calculated burning velocities. The model is found to be in good agreement with the present experiments in slowly burning flames, either in highly nitrogen diluted mixtures (Figure 3) or in very lean mixtures (Figure 5). Also burning velocities in very rich flames (Figure 4) are well reproduced. The calculations notably deviate from the experiments in the fast burning mixtures. The reason for the discrepancies observed should be in the remaining unknown deficiencies of the hydrogen combustion mechanism. However, the modeling was found in good agreement with fast burning velocities of hydrogen–air mixtures (Figure 1). Another possibility of additional experimental uncertainty, which cannot be totally excluded, is flame wrinkling. Formation of cellular flames and significant acceleration of the flame propagation speeds have been observed in similar experiments.[18] In the present work $H_2-O_2-N_2$ flames were invisible; therefore, the flatness of the flames was difficult to assess. An indication of the flatness is given by the temperature distribution in the burner plate which showed no anomalies that could arise in the case of cellular flames. Additionally, in our earlier experiments with diluted flames of $H_2 + CO + CO_2 + air$[19] which were stabilized on a similar burner and were visible, no cellularity has been observed. Also recent studies of hydrocarbon + oxygen + inert flames stabilized using the heat flux method[20] showed that cellularity does not appear in the mixtures with nitrogen as inert diluent.

At atmospheric pressure the flames are stabilized quite close to the burner, thus diffusion of active radicals toward the burner surface and reactions on it could potentially affect the flame structure and the measured burning velocity. These effects have been analyzed computationally[21] and experimentally[12,22] in hydrocarbon flames. It was concluded that reactions of hydrocarbon radicals on the burner surface have negligible influence on the formation of major and even minor products and thus on the laminar burning velocity. In hydrogen flames, however, diffusivity of the key H atoms is much higher than that of other species; therefore, a possible sink of H atoms on the surface was evaluated in the present work.

The modeling of this effect has been preformed employing the Chemkin code[15] and the detailed reaction mechanism outlined above. The mechanism was extended by the following reaction:

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(18) Konnov, A. A.; Dyakov, I. V. *Combust. Flame* **2004,** *136* (3), 371–376.

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(20) Konnov, A. A.; Dyakov, I. V. *Exp. Therm. Fluid Sci.* **2005,** *29,* 901–907.

(21) de Goey L. P. H.; Somers L. M. T.; Bosch W. M. M. L.; Mallens, R. M. M. *Combust. Sci. Technol.* **1995,** *104,* 387–400.

(22) Dyakov, I. V.; De Ruyck, J.; Konnov, A. A. *Fuel* **2007,** *86,* 98–105

$$Sc + H \rightleftharpoons ScH$$
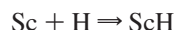
where Sc is an artificial scavenger of H atoms introduced in these calculations in a very small quantity (below a mole fraction of 10^{-4}) into the fresh mixture. The rate constant of this reaction and amount of scavenger was varied in such a way as to modify the concentration of H atoms at a distance corresponding to a local flame temperature of 360 K. One should recall that the flame was stabilized on a perforated plate, which was kept at this temperature (see Experimental Section). In fact, the physical principle of the flame stabilization on the heat flux burner resembles the computational principle of the adiabatic flame stabilization in an infinite domain as employed in the Chemkin code.[15] By fixing the temperature at one point in the flame-fixed coordinate system, the program calculates the laminar burning velocity as an eigenvalue. In the experiments, having the temperature of the fresh mixture of 298 K (controlled by the thermostatic jacket of the plenum chamber) the flame is stabilized at some distance where the temperature of the slightly preheated mixture coincides with the temperature of the burner plate. Thus the variation of H atoms concentration at the temperature point of 360 K in the modeling mimics a possible sink due to surface reactions.

The effect of a possible sink of H atoms on the surface is illustrated to be negligible for the fastest flame with oxygen content of 0.077 and equivalence ratio of 1.7. For this flame the calculated laminar burning velocity is 38.75 cm/s (cf. Figure 4). By introducing the assumption that all H atoms reaching the surface of the burner plate are removed from the system, the concentration of H should be reduced by less than about 30%. This value is estimated from the opening of the perforated pattern (Figure 2b) and by allowing a partial sink of H atoms inside holes of the perforated plate. In this case the calculated burning velocity is 38.72 cm/s. Even at the limiting case of a reduction of [H] by 60%, the calculated burning velocity is 38.67 cm/s. These tiny changes are well below the experimental uncertainties discussed above.

Conclusions

In the present investigation new measurements of the laminar burning velocity are presented and analyzed of flames propagating in hydrogen−oxygen−nitrogen mixtures by using the heat flux method. In the case of varying equivalence ratios these flames are measured with oxygen contents of $O_2/(O_2 + N_2) = 0.077$ and 0.1077. The measurements presented give an overall error in the laminar burning velocity which can be estimated to be about ±1 cm/s over a large range of equivalence ratios increasing up to ±3.1 cm/s for flames with very low heat release. The error estimate is smaller than ±0.8 cm/s with varying oxygen content at $\varphi = 1.058$. A comparison of the heat flux measurements with the experimental results obtained using the counterflow twin-flame technique[11] shows a discrepancy outside the experimental errors. Part of the discrepancy between experiments can probably be attributed to errors arising from the linear extrapolation to zero stretch rate, originally employed in ref 11. The new measurements of the burning velocities, which include error estimates, provide an extended basis for the validation of kinetic models.

Supporting Information Available: Reaction mechanism, including thermochemistry data. This material is available free of charge via the Internet at http://pubs.acs.org.