Laminar Flame Speeds and Kinetic Modeling of H₂/O₂/diluent Mixtures at Sub-atmospheric and Elevated Pressures

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Abstract:

Recognizing the need to improve the predictability of the foundational H₂/O₂ chemical kinetic mechanism over extensive parametric ranges of pressure, adiabatic flame temperature and composition, laminar flame speeds extracted from constant-pressure expanding flames were experimentally determined for H₂/O₂/diluent flames spanning the parameter range of: equivalence ratio from ultra-lean to ultra-rich (0.3 and 2.5), flame temperature from 1,300 to 2,200K, pressure from sub-atmospheric to elevated values of 0.25 to 20atm, and dilution of He up to 65% and CO₂ up to 34%. A new kinetic model, *HP-Mech*, based on evaluation of the rate coefficients from recent high-level quantum chemistry calculations and shock tube measurements, was developed and subsequently used to investigate the controlling reaction steps of these flames. In particular, the overall reaction order was extracted, allowing for the pressure dependence of the adiabatic flame temperature. The results show that it can assume values not only less than zero at high pressures, as was reported before, but also values larger than 2 at lower pressures. Sensitivity and reaction path analyses show that these responses are controlled by the competition between two opposing pathways involving reaction R9: H+O₂(+M)=HO₂(+M).

Keywords: Hydrogen flame speeds; Kinetic model; Reaction order; Sensitivity analysis; Reaction path analysis

1. Introduction

In spite of the foundational significance of hydrogen oxidation in combustion, there still exists considerable uncertainty in its oxidation mechanism. A prominent, recent demonstration of such inadequacy is the work of Li *et al.* [1], who explored the discrepancy between measured laminar flame speeds and model predictions, concluding that experimental uncertainty needs to be tightened in order to further improve the performance of the kinetic models. Such a scrutiny would require the acquisition of experimental data of high fidelity as well as extensive and extreme parametric coverages, especially those at sub-atmospheric and high pressures as well as using diluents other than nitrogen. Therefore, we present herein accurate measurements of laminar flame speeds covering both rich and lean mixtures of equivalence ratios (2.5 and 0.3), with a wide range of adiabatic flame temperatures (1300 to 2200K), pressures (0.25 to 20atm), and with helium (He) and carbon dioxide (CO₂) dilution. We shall also show that some of the literature experimental data at high pressures indeed require revision, as noted in [2].

Computationally, recognizing the recent advances of high-level quantum chemistry computations and the availability of shock tube rate measurements with laser diagnostics, we shall update the H₂/O₂ mechanism from the recent model of Burke *et al.* [3], hereafter referred to as *Model B*. The updated model is referred as the *HP-Mech*. We are particularly interested in the role of the third-body reaction R9: $\text{H} + \text{O}_2(+\text{M}) = \text{HO}_2(+\text{M})$, at low and high pressures. Indeed, we shall show in due course that while normally its global effect is to reduce the overall reaction order to be less than 2, it could actually elevate the overall reaction order to exceed 2 at sub-atmospheric pressures.

We shall now present the experimental specifications and results, which are followed by the development and validation of the kinetic model. With the new model, we shall then study the global implications and the detailed pathway structure of the reaction networks, leading to further understanding and enhanced utility of this important reactive system.

2. Experimental Specifications

All experiments were conducted in our well-vetted constant-pressure, dual-chamber apparatus [4, 5], which is uniquely suited for studies at extreme pressures away from the atmosphere. Table 1 lists the experimental conditions, including the equivalence ratio ϕ , adiabatic flame temperature T_f , total pressure P , and the corresponding mole fraction x_i for each component. The diluents were selected for the mixture to attain approximate unity Lewis number (Le), which is the ratio between thermal diffusivity and the controlling mass diffusivity, in order to reduce the uncertainty in flame speed extraction [6]. For rich H_2/O_2 mixtures, CO_2 was used as the diluent so as to reduce Le , avoid pulsating instability as well as examine the validity of H_2/O_2 kinetics with CO_2 kinetic effects, while for lean H_2/O_2 mixtures, helium was used to increase Le , hence reducing the influence of diffusional-thermal cellular instabilities.

Table 1. Experimental conditions. Initial temperature is 295($\pm$ 2)K.

ϕ	T_f (K)	P (atm)	x_{H_2}	x_{O_2}	x_{CO_2}	x_{He}
2.5	1500	1 to 20	0.5182	0.1036	0.3782	0.0000
2.5	1600	0.25 to 20	0.5495	0.1099	0.3406	0.0000
2.5	1700	1 to 5	0.5780	0.1156	0.3064	0.0000
2.5	1800	0.25 to 5	0.6061	0.1212	0.2727	0.0000
2.5	2000	0.25 to 1	0.6588	0.1318	0.2095	0.0000
2.5	2200	0.25 to 1	0.7092	0.1418	0.1489	0.0000
0.3	1300	1 to 2.5	0.0952	0.1587	0.0000	0.7460
0.3	1400	1 to 5	0.1071	0.1785	0.0000	0.7144
0.3	1500	1 to 5	0.1176	0.1961	0.0000	0.6863
0.3	1600	0.35 to 1	0.1305	0.2175	0.0000	0.6519
0.3	1800	0.25 to 1	0.1558	0.2597	0.0000	0.5844
0.3	2000	0.25 to 1	0.1863	0.3106	0.0000	0.5031

The flame front motion was recorded by a high-speed Schlieren image system, with the highest sampling rate of 15kHz at 600 pix $\times$ 600 pix, yielding the flame radius $R_f(t)$ and then the burned flame speed, $S_b(t) = dR_f/dt$. The laminar flame speed, without stretch, $S_{b,0}$, was then determined through extrapolation to zero stretch, using a nonlinear scheme with three fitting parameters, $S_b/S_{b,0} = 1 - 2L_b/R_f + C/R_f^2$ for rich cases and a linear scheme $S_b = S_{b,0} - L_b\kappa$ for lean cases [6], where L_b is the Markstein length and κ the stretch rate. The burned flame speed is divided by the density ratio between the unburned and burned gases to yield the unburned flame speed $S_{u,0}$. Furthermore, the reported mass burning rate f^0 is the product of $S_{u,0}$ and the density of the unburned mixture ρ_u .

The experimental results for rich and lean mixtures, at elevated and sub-atmospheric pressures, will be respectively presented in Figs. 1 to 4, and discussed when compared with the model calculations. We note in passing that with considerable thoroughness we have determined [2] that some of the high-pressure data of Refs. [7, 8], at 10atm and above, were obtained from flames exhibiting profuse flame-front cellular instability, which has led to higher values of flame speeds. It is suggested that these values be replaced by those reported herein.

3. An Updated H₂/O₂ Kinetic Mechanism (*HP-Mech*)

Based on the rate evaluations from recent fundamental measurements and theoretical predictions, the present H₂/O₂ model (available online [9]) inherits the same frame of Burke *et al.* [3] (*Model B*), with several key updates. First and foremost, reaction R9 was reevaluated based on the experimental data from Fernandes *et al.* [10] and Bates *et al.* [11], as well as the low-pressure limit rate of Michael *et al.* [12]. The derived rate coefficients by least square fitting of all the experimental data are generally 5~10% smaller than those employed in *Model B*. Secondly, we revisited the important reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ by incorporating the low-temperature rate measurements of $\text{OH} + \text{O} = \text{H} + \text{O}_2$. This update retains the high-temperature rate determined by Hong *et al.* [13] and Masten *et al.* [14] and therefore has very small effect on high-temperature oxidation, but is expected to affect the low-temperature reaction sequence in other applications. Thirdly, according to experiments and theoretical assessment on the uncertainty of $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$, the new rate expression is comprised of the two recommendations of Refs. [15, 16]. Lastly, we considered the falloff behavior of $\text{H} + \text{OH} (+\text{M}) = \text{H}_2\text{O} (+\text{M})$ by including the high-pressure limit rate and broadening factor from Sellevåg *et al.* [17], with the low-pressure limit rate fitted from available experimental measurements. The new rate is 20% smaller than the low-pressure limit of *Model B* and 50% higher than the low pressure limit of Sellevåg *et al.* There are additional modifications for the reactions: $\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$, $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$, $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$, and $\text{HO}_2 + \text{O} = \text{O}_2 + \text{OH}$, although they have only small effects on the flame speeds.

For CO₂ related reactions, we adopted the rate coefficients for CO+OH=H₂O+H as recommended in Joshi and Wang [18], which is 7% smaller than that used in Li *et al.* [1] (*Model L*) and USC Mech II. This reaction has been investigated both experimentally and theoretically, and very close agreements were found between them [18, 19, 20]. Consequently, the uncertainty of this reaction could be around 15%, which is much smaller than the 30% up-tuning in *Model L*. For the reaction H+HCO=H₂+CO, which was significantly modified in *Model L*, the rate coefficient in the present model is based on the experimental values of Friedrichs *et al.* [21] and the theoretical predictions by Harding *et al.* [22]. The rate used in *Model L* is essentially a factor of 2 higher than that in the present model. Finally, the rate coefficient of the reaction HCO(+M)=H+CO(+M) was adopted from Yang *et al.* [23] which investigated its non-RRKM behavior, with good agreements between the experiments and predictions in a broad range of pressures and temperatures.

4. Model Validation

The experimental measurements covering a wide parametric space were used to validate the present model. Figure 1 shows the mass burning rates for rich ($\phi=2.5$) H₂/O₂/CO₂ flames, at elevated pressures. Predictions from the present mechanism (*HP-Mech*), *Model L* [1] and NUI Galway mechanism (*Model G*) [24] are compared. It is seen that while all models perform well at lower pressures (<5atm), the prediction of the present model agrees better with the experimental results. At higher pressures (>10atm), all models show inadequate predictions, although the present model better captures the phenomenon of negative pressure dependence, which indicates that the mass burning rate decreases with increasing pressure [7, 25, 26, 27].

Figure 1. Mass burning rates for *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at *elevated pressures*. Symbols represent experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; red line is by *Model G* at 1600K.

Figure 2 shows the mass burning rates for lean ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames, at elevated pressures. It is noted that predictions by the *HP-Mech* not only agree relatively better with the present experiments, but they also capture the negative pressure response [8, 25, 26, 27].

Figure 2. Mass burning rates for *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at *elevated pressures*. Symbols represent experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; blue line is by *Model B* at 1400K; red line is by *Model G* at 1400K.

Figures 3(a) (b) show the mass burning rates and laminar flame speeds for rich ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at sub-atmospheric pressures. It is seen that predictions by the present model (*HP-Mech*) and *Model L* fall within the experimental error bar at higher temperatures ($>1800\text{K}$). However, for the very low pressure ($<0.4\text{atm}$) and low temperature ($<2000\text{K}$) conditions, the predictions of *HP-Mech* agree better with the experimental results.

Figure 3. Mass burning rates (a) and laminar flame speeds (b) for *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at *sub-atmospheric pressures*. Symbols represent present experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; red line is by *Model G* at 1800K . The inserted figure in (a) is to avoid cluttering.

Figures 4(a) (b) show the mass burning rates and laminar flame speeds for lean ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at sub-atmospheric pressures. It is seen that, except for the cases with ultra-low pressure (0.25atm) and certain temperatures (2000K for *HP-Mech*, 1800K for *Model L*), predictions of the present model (*HP-Mech*) and *Model L* are within the experimental error bars. Since *HP-Mech* inherits *Model B*, their predictions are similar.

Figure 4. Mass burning rates (a) and laminar flame speeds (b) for *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at *sub-atmospheric pressures*. Symbols represent present experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; blue line is by *Model B* at 1800K; red line is by *Model G* at 1800K.

5. Analysis of Reaction Networks

Recognizing the essential role of reaction R9 on the pressure dependence of the H_2/O_2 system, and through it the dependence on other system parameters, we shall first assess the response of such global parameters such as the activation energy and reaction order with extensive parametric variations. We shall then present the corresponding sensitivity and pathway analyses to show the connections in the kinetic network.

5.1 Overall reaction order and activation energy

The mass burning rate is given by $f^0 \sim P^{n/2} \exp(-E_a/2R_0T_f)$, with the overall reaction rate scales with $\omega \sim P^n \exp(-E_a/R_0T_f)$, where n is the overall reaction order, E_a the overall activation energy, and R_0 the universal gas constant [25]. Since $S_{u,0} = f^0/\rho_u \sim f^0/P$, the laminar flame speed scales with $S_{u,0} \sim P^{n/2-1} \exp(-E_a/2R_0T_f)$. Consequently, the mass burning rate increases with pressure for $n > 0$, while the laminar flame speed increases with pressure for $n > 2$.

Using the expression for the mass burning rate, the reaction order has usually been extracted [25] as $n = 2\partial \ln f / \partial \ln P$. Implicit in this evaluation is the assumption that the adiabatic flame temperature, T_f ,

does not vary with pressure. It is, however, well recognized that while T_f indeed depends only weakly on pressure, the dependence can become stronger at reduced pressures due to increased dissociation. Consequently, the dissociation effect needs to be subtracted out when determining the overall reaction order as defined. Thus with T_f as $T_f(P)$, the T_f -compensated reaction order is evaluated as,

$$n' = n - \frac{E_a}{R_0} \frac{P}{T_f^2} \frac{\partial T_f}{\partial P} \quad (1)$$

Thus, in this revised expression, the overall activation energy is calculated as $E_a = -2R_0 \partial \ln f / \partial (1/T_f)$ [25]. The calculated activation energies and reaction orders are shown in Fig. 5.

Figure 5. Calculated (a) global activation energies and (b) reaction orders for different mixtures at various pressures: *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at 1600K and 2000K are in blue and red, respectively; *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at 1600K and 2000K are in black and green, respectively. Dash and solid lines for the overall reaction orders are calculated by assuming T_f is constant and $T_f(P)$, respectively.

The extracted values of E_a and n show considerable variation over the parametric ranges of concentration, pressure, and adiabatic flame temperature, and that the reaction order decreases with pressure and has the tendency to assume negative values, corresponding to the negative pressure dependence in Figs. 1 and 2. Furthermore, the present results show the following interesting features for

sub-atmospheric flames. First, Fig. 5(a) shows that E_a of rich mixtures (red and blue lines) are much smaller than those of lean mixtures (black and green lines), implying rich mixtures have less energy barriers to overcome and thus less temperature dependence than lean mixtures. Second, Fig. 5(b) shows that, at lower pressures ($<0.5\text{atm}$), n for rich mixture ($\varphi=2.5$) at both low and high temperatures (1600 and 2000K) are larger than 2, while those for lean mixtures at similar conditions approach $n \approx 2$. These interesting responses of the overall reaction order are related to the opposing role of reaction R9 at high and low pressures, as demonstrated through the following sensitivity analysis.

5.2 Sensitivity analysis

The conditions with the uncommon overall reaction orders ($n > 2$ or < 0) are selected to conduct the following sensitivity analysis. Figure 6 shows the sensitivity of mass burning rate to A-factors of the important elementary reactions. For each case, the sensitivity of each reaction is normalized by its largest absolute sensitivity. Since the cases at high pressure (15atm) have been studied before [7, 8], the focus is on the low pressure cases (0.5atm).

Figure 6. Normalized sensitivity of mass burning rate to A-factors of elementary rates for (a) rich ($\varphi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames and (b) lean ($\varphi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames.

Figure 6(a) shows the sensitivity analysis for rich mixtures ($\phi=2.5$). It is noted that while the sensitivity of reaction R9 is negative at high pressures (15atm), it becomes positive at low pressures (0.5atm). While the behavior at high pressures is to be expected, demonstrating the chain terminating nature of this reaction, and is the cause of the $n < 0$, negative pressure dependence noted and identified previously, this third-body reaction reverses its terminating role at low pressures and actually promotes the global reactivity, with $n>2$, as shown in Fig. 5 (b). The HO₂ radical now participates in the strong chain carrying reaction HO₂+H=OH+OH, leading to enhanced reactivity.

Figure 6(b) shows the sensitivity on lean mixtures ($\phi=0.3$). At high pressures (15atm), the termination effect of reaction R9 is obvious. However, at low pressures (0.5atm), since the collision efficiency of He is lower than CO₂, the role of this reaction is not as significant as the rich cases in Fig. 6(a).

5.3 Reaction path analysis

Sensitivity analysis shows the promoting/retarding role of each elementary reaction, which needs reaction path analysis to connect the various important reactions for further exposition. Figure 7 shows the calculated reaction path for rich and lean mixtures ($\phi=2.5$ and 0.3), with adiabatic flame temperature of 2000K at different pressures (0.5atm and 15atm). To study the opposing roles of reaction R9 in different circumstances, the major reactions related to HO₂ are marked in the figures. The percentage of reactants following the specific reaction path is also shown next to its reaction pathways.

Figure 7. Calculated reaction pathways for $\text{H}_2/\text{O}_2/\text{diluent}$ flames at 2000K: upper figures are *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at (a) 0.5atm and (b) 15atm, respectively; lower figures are *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at (c) 0.5atm and (d) 15atm, respectively. The percentage of the reactant following specific reaction path is shown by the numbers next to the reaction pathway.

Figures 7(a) (b) show the reaction path analysis on rich $\text{H}_2/\text{O}_2/\text{CO}_2$ mixtures at different pressures. First, starting from the reactant, O_2 is converted to HO_2 through reaction R9. Then, there are two pathways for HO_2 . One is from HO_2 back to H_2 by reaction $\text{HO}_2 + \text{H} = \text{O}_2 + \text{H}_2$, with the overall retarding effect of $\text{H} + \text{H} = \text{H}_2$. The other is from HO_2 to OH through $\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$, with the overall effect of $\text{H} + \text{H} + \text{O}_2 = \text{OH} + \text{OH}$. This chain carrying reaction could promote the overall reactivity in two aspects: Chemically, OH could be more important than the abundant H because it can crack H_2 and generate the product H_2O through $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$ and $\text{H} + \text{OH} (+\text{M}) = \text{H}_2\text{O} (+\text{M})$, respectively. Thermally, R9 and $\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$ release large amount of heat, which further facilitates the global reactions. Therefore, the role of this reaction pathway is to promote the overall reactivity. The sensitivity of the common

reaction R9 is the result of competition between the two pathways. In the low pressure case in Fig. 7(a), more HO₂ (80%) follows the promoting pathway through HO₂+H=OH+OH, instead of retarding reaction pathway through HO₂+H=O₂+H₂, than that in the high pressure case (71%) in Fig. 7(b). Consequently, the sensitivity of reaction R9 is positive at low pressures, and becomes negative at high pressures, as shown in Fig. 6(a).

Figures 7(c) (d) show the result of reaction path analysis on lean H₂/O₂/He mixtures at different pressures. Similar to the rich cases mentioned before, the opposing sensitivity of reaction R9 is the competition results between two reaction pathways. The promoting one is still R9 and HO₂+H=OH+OH with the overall effect of H+H+O₂=OH+OH. The other one is R9 with HO₂+OH=O₂+H₂O and HO₂+O=O₂+OH. Such reaction pathway reduces the global reactivity because the overall effect is H+OH=H₂O or H+O=OH, which either consume the important H and generate the product H₂O, or convert O into OH, instead of cracking the reactant O₂. In the low pressure case in Fig. 7(c), more HO₂ (42%) follows the promoting pathway, instead of the retarding pathway, than that in the high pressure case (22%) in Fig. 7(d). Consequently, the sensitivity of reaction R9 is positive at low pressures and negative at high pressures, as shown in Fig. 6(b).

6 Conclusions

The present study has advanced our knowledge of the foundationally important H₂/O₂ reaction system in the following aspects. First, recognizing the inadequacy of some of the recent high-pressure flame speed data, and the absence of sub-atmospheric pressure flame speed data, we have acquired flame speed data over extensive system parametric ranges of pressure, adiabatic flame temperature, mixture composition, and with CO₂ dilution. Second, using the evaluated rate coefficients based on recent experimental determination and theoretical predication, we have updated the kinetic model for the H₂/O₂/diluent system, referred as the *HP-Mech*, and compared it with the new flame speed data. Third, using this validated model, we have explored the flame response in terms of the global activation energy

and global reaction order, n , and show that not only n can assume negative values at high pressures through the termination role of reaction R9: $\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$, as originally demonstrated in Ref. [26], but it can also assume values greater than 2 at low pressures through the promoting role of R9. Finally, using sensitivity and pathway analyses we have identified the specific, separate routes through which the product HO_2 from R9 manifests induces the opposing response.

Acknowledgments

This collaborative work between the research groups of Chung K. Law and Yiguang Ju was supported by the Combustion Energy Frontier Research Center, an Energy Frontier Research Center funded by the US Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0001198; an NETL UTSR Program, also of the US Department of Energy, under Award Number DE-FE0011822; an NSF program under the technical management of Dr. S.C. Kong; and an AFOSR program under the technical management of Dr. Mitat Birkan.

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Table 1. Experimental conditions. Initial temperature is $295(\pm 2)\text{K}$.

φ	$T_f (K)$	P (atm)	x_{H_2}	x_{O_2}	x_{CO_2}	x_{He}
2.5	1500	1 to 20	0.5182	0.1036	0.3782	0.0000
2.5	1600	0.25 to 20	0.5495	0.1099	0.3406	0.0000
2.5	1700	1 to 5	0.5780	0.1156	0.3064	0.0000
2.5	1800	0.25 to 5	0.6061	0.1212	0.2727	0.0000
2.5	2000	0.25 to 1	0.6588	0.1318	0.2095	0.0000
2.5	2200	0.25 to 1	0.7092	0.1418	0.1489	0.0000
0.3	1300	1 to 2.5	0.0952	0.1587	0.0000	0.7460
0.3	1400	1 to 5	0.1071	0.1785	0.0000	0.7144
0.3	1500	1 to 5	0.1176	0.1961	0.0000	0.6863
0.3	1600	0.35 to 1	0.1305	0.2175	0.0000	0.6519
0.3	1800	0.25 to 1	0.1558	0.2597	0.0000	0.5844
0.3	2000	0.25 to 1	0.1863	0.3106	0.0000	0.5031

Figure Captions:

Figure 1. Mass burning rates for *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at *elevated pressures*. Symbols represent experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; red line is by *Model G* at 1600K.

Figure 2. Mass burning rates for *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at *elevated pressures*. Symbols represent experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; blue line is by *Model B* at 1400K; red line is by *Model G* at 1400K.

Figure 3. Mass burning rates (a) and laminar flame speeds (b) for *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at *sub-atmospheric pressures*. Symbols represent present experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; red line is by *Model G* at 1800K. The inserted figure in (a) is to avoid cluttering.

Figure 4. Mass burning rates (a) and laminar flame speeds (b) for *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at *sub-atmospheric pressures*. Symbols represent present experimental results. Solid lines are model predictions: green lines are by current model; purple lines are by *Model L*; blue line is by *Model B* at 1800K; red line is by *Model G* at 1800K.

Figure 5. Calculated (a) global activation energies and (b) reaction orders for different mixtures at various pressures: *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at 1600K and 2000K are in blue and red, respectively; *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at 1600K and 2000K are in black and green, respectively. Dash and solid lines for the overall reaction orders are calculated by assuming T_f is constant and $T_f(P)$, respectively.

Figure 6. Normalized sensitivity of mass burning rate to A-factors of elementary rates for (a) *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames and (b) *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames.

Figure 7. Calculated reaction pathways for $\text{H}_2/\text{O}_2/\text{diluent}$ flames at 2000K: upper figures are *rich* ($\phi=2.5$) $\text{H}_2/\text{O}_2/\text{CO}_2$ flames at (a) 0.5atm and (b) 15atm, respectively; lower figures are *lean* ($\phi=0.3$) $\text{H}_2/\text{O}_2/\text{He}$ flames at (c) 0.5atm and (d) 15atm, respectively. The percentage of the reactant following specific reaction path is shown by the numbers next to the reaction pathway.