RICH METHANE/AIR FLAMES: BURNING VELOCITIES, EXTINCTION LIMITS, AND FLAMMABILITY LIMIT

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Rich Methane/Air Flames: Burning Velocities, Extinction Limits, and Flammability Limit

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Abstract

A theoretical investigation has been conducted to establish a reliable chemical kinetic mechanism that can determine the extinction limit of opposed-flow, strained, rich premixed methane-air flames. In the process of developing this kinetic representation for rich methane-air flames, we found that the heat of formation of $^1CH_2 = 102.5$ kcal/mole, which is 1 kcal/mole higher than the currently available thermochemical data, gives the best agreement with experimental data on burning velocities for equivalence ratios between 0.5 and 1.7. Employing this value for $\Delta H_f(^1CH_2)$ in our calculations, the extinction stretch rate, K_{ex} , was found to be $K_{ex} = 2250 \text{ sec}^{-1}$ for $\phi = 1.0$, $K_{ex} = 2000 \text{ sec}^{-1}$ for $\phi = 1.1$, and $K_{ex} = 1400 \text{ sec}^{-1}$ for $\phi = 1.2$. These results agree better with experiments than those using a lower heat of formation of singlet methylene. In comparison with previous calculations made by Kee et al., our predictions are basically the same except that our extinction stretch rate is slightly higher at $\phi = 1.0$ and that our location of the maximum extinction stretch rate is closer to that found in experiments. In addition, we establish the rich flammability limit using two different criteria to be approximately between $\phi = 1.61$ and $\phi = 1.68$, which agrees very well with an experimental value of $\phi = 1.67$.

*Post-doctoral Appointee

Introduction

Understanding the structures and extinction conditions of combustion processes continues to be a challenging problem due to the chemical and fluid mechanical complexities involved. In recent years, thanks to the advance of computing technology, mathematical modeling has become a very useful and even essential tool in predicting the structures and critical conditions, as well as in determining the principal chemical paths of many combustion systems using detailed chemistry. In this paper, we present our findings in the continuing research of premixed methane-air flames.

Previously, the chemical kinetic mechanism used by Kee et al. [1], which came from Miller and Bowman [2], produced high burning velocities under rich conditions [3]. As a result of these more robust rich flames, the extinction stretch rates, K_{ex} , calculated by Kee et al. [1] for an opposed-flow, strained premixed flame, were significantly higher than those measured by Law et al. [4]. These findings provide the impetus for developing a more reliable mechanism to predict accurately the extinction limit for rich methane-air flames. In order to accomplish this goal, we first need to assess how well this mechanism performs in freely propagating systems, since if it cannot accurately predict burning velocities, there is no reason to believe that it will produce correct critical extinction conditions. In the process of constructing this kinetic representation, we discovered that ΔH_{f1CH_2} plays a significant role in the determination of burning velocities and extinction limits of methane-air flames. This occurs because of the very fast reaction $^1CH_2 + H_2O \rightleftharpoons CH_3 + OH$, whose rate coefficient has been determined by Hack, et al. [5] to be nearly collision frequency at room temperature. In our model, we input the reaction as written with Hack's rate coefficient ($^1CH_2 + H_2O \rightarrow CH_3 + OH$), but the reverse direction of this reaction actually takes place in methane flames, thus causing the thermochemistry (through the equilibrium constant, which is used to calculate the reverse rate) to have a direct effect on the kinetics. The situation is further complicated by the fact that, using the best available thermochemistry, one would calculate this singlet methylene reaction with water to be about 0.5 kcal/mole endothermic. Clearly this is not consistent with such a fast reaction, and use of this thermochemistry with Hack's rate coefficient will result in a rate for $CH_3 + OH \rightarrow ^1CH_2 + H_2O$ that is too fast.

To address the validity issue of the new mechanism, we employ mathematical modeling to determine the structure and burning velocity of freely propagating methane-air systems and compare these results with experimental data for a range of equivalence ratios from 0.5

to 1.7 at atmospheric pressure. Sensitivity and reaction rate analyses were also performed to provide further insight into the chemical behavior and principal path of oxidation, as well as the flammability limit of these rich flames. In our calculations, we test 3 different values for the heat of formation for 1CH_2 : a) the currently accepted value of $\Delta H_{f^1CH_2} = 101.5$ kcal/mole, b) a high value of $\Delta H_{f^1CH_2} = 104.5$ kcal/mole. and c) an intermediate value of $\Delta H_{f^1CH_2} = 102.5$ kcal/mole. Comparison with experiments [6,7] reveal that the intermediate value for $\Delta H_{f^1CH_2} = 102.5$ kcal/mole gives the best agreement for burning velocity predictions. This value of the heat of formation of singlet methylene is then used in extinction limit calculations for an opposed-flow, strained methane-air premixed flame for $\phi = 1.0$, $\phi = 1.1$, and $\phi = 1.2$, and the results were compared with Law's experiments [4]. In addition, we also attempted to establish the flammability limit of rich methane/air flames using two different criteria: a) the composition that yields $V_u = 5$ cm/s (a qualitative rule proposed by Westbrook [8] and b) a kinetic criterion reported by Law and Egolfopoulos [9], where the competition between branching and termination reactions is considered.

Formulation for the numerical problem

Chemical Kinetic Mechanism

The present kinetic scheme is derived mostly from Miller and Melius [10] with some improvements. The main modifications are the following:

1. The new rate used for the most important chain branching reaction $OH + O = H + O_2$ comes from Masten et al. [11]; this rate coefficient is consistent with Hessler's measurements at very high temperature [12] and also agrees with Miller's trajectory calculations using Varandas's potential energy surface over a very wide temperature range. The rate expression $k_f = 2.02 \times 10^{14} T^{-0.4}$ cm³/mole-sec appears to represent the kinetic data available from below room temperature to above 5000 K [13], where the subscript f denotes the forward direction of the reaction.
2. The inclusion of the methanol subset, which is comprised mostly of compilations by W. Tsang, the National Institute of Standards and Technologies [14], and the European group (CEC) [15], with the use of Choudhury's rate for reaction $CH_3O + M = CH_2O + H + M$ [16].

This new scheme consists of 239 reactions involving 53 chemical species (including up to C_6 chemistry). Due to the length restriction, the mechanism is not listed here but can be obtained from the authors.

Governing Equations

Freely Propagating Premixed Flame

The mathematical formulation for a steady, planar, adiabatic deflagration at low Mach number has been extensively cited in the literature [17,18] and will not be presented here. The mass flow rate $\dot{M}$ is an eigenvalue and must be determined as part of the solution; therefore, in addition to the usual boundary conditions, the location of the flame is chosen to be fixed by specifying the temperature at one point. This is sufficient to obtain the solution for the flame speed eigenvalue. As an improvement over the previous formulation, thermal diffusion and multicomponent transport [19] are included, and central differencing techniques are employed.

Strained, Opposed Premixed Flame

Figure 1 is an illustration of the configuration used in modeling strained, opposed premixed flames; the detailed description can be found in Ref. [1]. The mixture composition, temperature, and the inlet velocity are specified at the nozzle exit and symmetry conditions are applied at the stagnation or symmetry plane. The nozzle separation distance for the present calculations is 7mm. In this fixed-domain approach, inlet velocity is purely axial at $x = -L$, and the radial pressure gradient eigenvalue is computed. The extinction limit is calculated with the aid of the arc length continuation method. Figure 2 illustrates this method using a plot of some characteristic of the solution (maximum flame temperature) as a function of some parameter (velocity). Given a solution at point 1, the goal is to calculate the solution at point 2 efficiently. Using the normalized arc length continuation method, the relationship between point 1 and point 2 can be written as:

$$\Delta s = \sqrt{\left(\frac{T_{max,2} - T_{max,1}}{T_{max,1}}\right)^2 + \left(\frac{U_2 - U_1}{U_1}\right)^2}. \quad (1)$$

This procedure involves a change of variables, where the independent parameter (velocity) becomes a dependent variable, and the arc length Δs becomes the parameter. Equation (1)

is then solved together with the other governing equations for a specified value of Δs (which decreases in value as the extinction limit is approached). The most important feature of the continuation procedure is its behavior near the extinction limit—a turning point in the solution (where vertical tangency occurs in Fig. 2). At this point, the Jacobian of the original system is singular, whereas the Jacobian of the augmented system is well behaved. Therefore, this method is a great tool in accurately predicting flame extinction limits.

Results and Discussions

Burning Velocity

Under stoichiometric and slightly rich conditions, reaction with OH is the dominant removal path for methyl radicals; this reaction $CH_3 + OH \Rightarrow$ products has several channels; the most important of them include:

The first five paths are included in our mechanism, and of these, reaction (4) is the most important under flame conditions. Reaction (6) has only recently been introduced by Walch [20] as a possibility from electronic structure calculations. The sensitivity analysis for the mass burning rate of a freely-propagating methane-air premixed flame for the equivalence ratio of 1.6 shown in Fig. 3 reveals that the reaction $CH_3 + OH = {}^1CH_2 + H_2O$ plays an important role, due to the abundance of methyl radicals under rich conditions. In 1988, Hack et al. [5] measured the reverse path of this reaction, i.e., ${}^1CH_2 + H_2O \rightarrow CH_3 + OH$, and found it to be approximately gas kinetic at room temperature (on the order of $\sim 10^{14}$ cm³/mol-sec). In our model, we include this reaction as measured by Hack in the (-4) direction; however, in methane flames this reaction actually proceeds in the forward (4) direction. In our flame calculations, reverse rates are determined from equilibrium constants and forward rates; this fact causes the thermochemistry to have a direct effect on kinetics.

Furthermore, from the best available thermochemical data, one could determine reaction (-4) to be approximately 0.5 kcal/mole endothermic. This is not consistent with such a large rate coefficient. Later, in 1992, Oser et al. [21] performed direct measurements of reaction (4) for a range of temperatures from 300-480 K. They investigated the 1CH_2 product channel by measuring the mole fraction of 1CH_2 radicals and the increase in H_2O signal upon reaction, and, by combining the results from Hack et al. [5] for the reverse reaction and their own observation for the forward path, Oser et al. [21] concluded that the heat of formation of 1CH_2 should be $\Delta H_{f^1CH_2} = 103.9$ kcal/mole. This conclusion motivated us to test several values of the heat of formation for 1CH_2 because, although the separation energy for $^3CH_2 \rightarrow ^1CH_2 \sim 9$ kcal/mole is fairly reliable and accepted [22], the error limit for the heat of formation of triplet methylene is subject to some uncertainty [23,24]. The three values used are (a) the currently accepted value of $\Delta H_{f^1CH_2} = 101.5$ kcal/mole, (b) a high value of $\Delta H_{f^1CH_2} = 104.5$ kcal/mole, and (c) an intermediate value of $\Delta H_{f^1CH_2} = 102.5$ kcal/mole. The heats of formation of triplet methylene (CH_2) were appropriately changed to correspond with those of singlet methylene using the separation energy of ~ 9 kcal/mole.

Figure 4 represents the burning velocity as a function of equivalence ratio ϕ . Theoretical predictions are compared with experimental data from Yu et al. [6] (denoted by filled circles) and Yamaoka and Tsuji [7] (denoted by diamonds). The smooth line represents calculations using $\Delta H_{f^1CH_2} = 101.5$ kcal/mole and $\Delta H_{f^3CH_2} = 92.5$ kcal/mole; the dotted line, a higher value of the heat of formation for $\Delta H_{f^1CH_2} = 104.5$ kcal/mole and $\Delta H_{f^3CH_2} = 95.5$ kcal/mole, and the star symbols (*), an intermediate value of the heat of formation for $\Delta H_{f^1CH_2} = 102.5$ kcal/mole and $\Delta H_{f^3CH_2} = 93.5$ kcal/mole. From this plot, it is abundantly clear that there is a direct relationship between the burning velocity of methane-air flame and $\Delta H_{f^1CH_2}$ from lean to rich conditions. It is also easily observed that the intermediate value of $\Delta H_{f^1CH_2}$ results in the best match with experimental data. Given the uncertainty in determining this quantity, it is worthwhile to entertain the possibility that $\Delta H_{f^1CH_2} \sim 102.5$ kcal/mole, which is closer to the value suggested by Oser et al. [21] than that currently used.

Flammability Limit

Although the definition of the flammability limit is clear, i.e., the state at which steady propagation of the one-dimensional, planar premixed flame in the doubly-infinite domain fails to be possible [25], the theoretical determination of such a limit remains problematical.

It is not clear when and if such a limit even exists theoretically. In this work, we compare two limits based on different criteria:

1. the critical composition which produces a burning velocity of 5 cm/s (Because the model is adiabatic, it will continue to calculate flame propagation at any equivalence ratio, although the burning velocity will be small; Westbrook [8] reported a qualitative rule that $V_u < 5$ cm/s corresponds to a nonflammable mixture.)
2. the critical composition where the rate of the primary chain-termination reaction is equal to that of the chain-branching reaction (Law and Egolfopoulos [9]).

Employing the above criteria, we observe from Fig. 4 (star symbols) that $\phi = 1.68$ renders a burning velocity of 5 cm/s. To use Law's criterion, which is based on the concept that competition between branching and termination reactions must be important for the weakly-reacting flames close to the flammability limits, a sensitivity analysis was conducted for a rich condition ($\phi = 1.6$) to establish the most important chain-branching and chain-termination reactions. Figure 3 shows that these reactions are $H + O_2 \rightarrow OH + O$ and $CH_4 + H \rightarrow CH_3 + H_2$, respectively. Once the dominant branching and termination paths are identified, it is found that their respective rate profiles approach each other at the flammability limit. This observation can be seen in Fig. 5, which presents the temperature at the maximum rate of each reaction as a function of equivalence ratio. In order to establish a quantitative critical composition, a parameter α (termed the "flammability exponent") was proposed by Law and Egolfopoulos [9] to be $\alpha = \partial(\ln\omega_T)/\partial(\ln\omega_B)$, where $\omega \equiv$ net rate, and T and B denote termination and branching, respectively. The critical composition where $\alpha = 1$ represents the flammability limit, and from our calculations, $\alpha = 1$ at $\phi = 1.62$. This value agrees very well with Law's experiments ($\phi = 1.67$) and calculations ($\phi = 1.69$). It is interesting to note that two different definitions yield very similar results; it is safe to say at $\phi > 1.68$, methane-air flames will not propagate at atmospheric pressure.

Figure 5

Extinction Limits

For the opposed-flow, strained premixed flame computations, a stretch parameter K is defined as the maximum axial velocity gradient $-du/dx$, as shown in Fig. 6. The velocity profile in Fig. 6 is initially that of a stagnation flow characterized by the specified negative slope. It reaches a minimum, then increases due to thermal expansion, and finally,

Figure 6

when heat release is complete, it decreases in accordance with the stagnation flow requirement. Figure 7 shows maximum flame temperature as a function of the reciprocal stretch rate, $1/K$, for methane-air flames. A vertical tangent can be drawn where the flame is extinguished, and Fig. 7 gives a value of $K_{ex} = 2700 \text{ sec}^{-1}$ and $T_{max} = 1763 \text{ K}$ for a stoichiometric methane-air flame and $K_{ex} = 2600 \text{ sec}^{-1}$ and $T_{max} = 1814 \text{ K}$ for $\phi = 1.1$ using $\Delta H_{f1CH_2} = 101.5 \text{ kcal/mole}$ and $\Delta H_{f3CH_2} = 92.5 \text{ kcal/mole}$, while $\Delta H_{f1CH_2} = 102.5 \text{ kcal/mole}$ and $\Delta H_{f3CH_2} = 93.5 \text{ kcal/mole}$ yield $K_{ex} = 2250 \text{ sec}^{-1}$ and $T_{max} = 1775 \text{ K}$ for $\phi = 1.0$, $K_{ex} = 2000 \text{ sec}^{-1}$ and $T_{max} = 1824 \text{ K}$ for $\phi = 1.1$, and $K_{ex} = 1400 \text{ sec}^{-1}$ and $T_{max} = 1854 \text{ K}$ for $\phi = 1.2$. Comparison of the present model with experiments made by Law, et al. [4], which give a value of $K_{ex} = 1650 \text{ sec}^{-1}$ for methane-air flame at $\phi = 1.0$, $K_{ex} = 1250 \text{ sec}^{-1}$ at $\phi = 1.1$, and $K_{ex} = 750 \text{ sec}^{-1}$ at $\phi = 1.2$ shows better agreement for the higher heats of formation. In comparing with previous calculations made by Kee et al. [1], our model gives basically the same results except that our extinction stretch rate is slightly higher at $\phi = 1.0$, and the location of the maximum extinction stretch rate in our calculations matches that of experiments better. An interesting point to note here is that the peak burning velocity for a freely-propagating premixed methane-air flame occurs at about $\phi = 1.1$ and the peak K_{ex} for an opposed-flow, strained flame occurs at a slightly leaner condition; this observation was found for both experiments and calculations.

Judging from the comparisons, one can observe that although there is good qualitative agreement, there is still a quantitative difference. Kee et al. [1] proposed several possibilities for the discrepancy. The first is that the experimental measurements are made for varying nozzle separations, which are not specifically reported, and this may not be modeled accurately in our calculations since our separation distance was fixed at 7 mm. A second reason may be that we have modeled the flow exiting the nozzles as a simple plug flow where, in reality, there may be some radial spreading at the nozzle exit. A third reason for the discrepancy may lie in the method of calculating K_{ex} ; this method is employed in both experiments and models and requires some judgment to decide exactly where to define the axial velocity gradient. In the simulations, we observe that there can be a $\geq 100 \text{ sec}^{-1}$ variation in the velocity gradients depending on exactly where they are evaluated. Thus, some disagreement seems inevitable in this comparison.

Concluding Remarks

In the present investigation, we have reported our efforts in developing a reliable kinetic representation that can accurately predict the extinction limits of rich methane/air flames. During this process, we observed that the heat formation of 1CH_2 significantly influences the determination of the burning velocity; a change of only 1 – 3 kcal/mole results in an average of 2 – 7 cm/s difference in burning velocity from lean to rich conditions. We established that a value of $\Delta H_{f^1CH_2} \sim 102.5$ kcal/mole and $\Delta H_{f^3CH_2} \sim 93.5$ kcal/mole give the best agreement between modeling and experiments. Thus, this change was incorporated into our mechanism, which consists of 239 reactions involving 53 chemical species. Our predictions of the extinction limit for 3 equivalence ratios, $\phi = 1.0$, $\phi = 1.1$, and $\phi = 1.2$ reveal better agreement with experiments if this intermediate value of the heat of formation of 1CH_2 is used, although there is still a discrepancy in the quantitative comparison which requires further investigation. Flammability limits were also determined using two different criteria, and both yield values which are essentially comparable to one another; what this means is that at $\phi \geq 1.68$, methane-air flames will not propagate under atmospheric pressure.

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List of Figures

1. Figure 1. Illustration of the configuration used in modeling strained, opposed flow premixed flames
2. Figure 2. Plot of maximum flame temperature as a function of velocity.
3. Figure 3. Sensitivity for the mass burning rate for freely propagating premixed flame.
4. Figure 4. Burning velocity as a function of equivalence ratio ϕ for freely propagating premixed flame.
5. Figure 5. Temperature at maximum branching and termination rate as a function of equivalence ratio.
6. Figure 6. Axial velocity profile of a strained premixed flame.
7. Figure 7. Maximum flame temperature as a function of the reciprocal stretch rate, $1/K_{ex}$, for $\phi = 1.0, 1.1$, and 1.2 methane-air premixed flame.

Figure 1

Figure 2

Methane-Air Premixed Flame

Methane-Air Premixed Flame

Opposed-Flow, Strained Methane
Premixed Flame

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