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Effects of Ethylene Addition on Counterflow Ignition and Flame Propagation in Methane/Ethylene Mixtures

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The ignition temperatures of nitrogen-diluted mixtures of methane and ethylene were measured by counterflowing heated air up to 3atms. In addition, the laminar flame speeds of air, methane and ethylene mixtures were obtained in the counterflow system under atmospheric pressure, for extensive ranges of lean-to-rich equivalence ratio. These experimental data, relevant to low-temperature ignition chemistry and high-temperature flame chemistry, were subsequently compared with calculations using two detailed ethylene mechanisms consisting of 70 and 75 species respectively. Sensitivity and Computational Singular Perturbation (CSP) analyses were applied to identify the role of ethylene addition in facilitating nonpremixed ignition and promoting premixed flame propagation. Furthermore, by studying the ignition response and flame propagation of these mixtures of hydrocarbons of the same family but with quite different reactivities, the hierarchical nature of the associated oxidation kinetics was assessed. This issue was further examined by comparing the sizes of the reduced mechanisms of the pure fuels and their mixtures.

1. Introduction

Counterflow ignition temperatures and laminar flame speeds are important global combustion response parameters in the study of the low- and high-temperature hydrocarbon oxidation as well as in developing comprehensive kinetic mechanisms. Extensive studies on these subjects have been conducted for small hydrocarbon fuels. Specifically, ignition temperatures in the nonpremixed counterflow were measured by Fatache et al. [1-2] for the simplest species, namely hydrogen and methane, and by Zheng [3] for the C2-C4 alkenes. Laminar flame speeds were measured using different techniques including that of the counterflow twin flame for the C1-C8 hydrocarbons [4-8]. However, there are relatively few studies on fuel mixtures. Most of the studies were on hydrogen addition to hydrocarbon fuels in order to promote ignition and enhance the burning intensity. For example, Law and co-workers studied the counterflow nonpremixed ignition of H₂/CH₄ and H₂/CO mixtures [9-11], and measured the laminar flame speeds of H₂/CH₄ and H₂/C₃H₈ mixtures in adiabatic, counterflows [12].

The present study was motivated to understand the effects of ethylene addition in fuel mixtures. Here we first note that the ignitability and burning velocities of ethylene are greater than those of alkanes, which are the major components in practical fuel mixtures and blends. Hence it can be considered to be used in various ways to enhance the performance of other gaseous or liquid fuels. The enhancement is expected to be particularly prominent for methane which, being the major constituent of natural gas, poses considerable challenges for its utilization in practical devices because of its low ignitability and burning intensity.

In view of the above considerations, the first goal of this study was to acquire experimental data on ignition temperatures in nonpremixed diffusive system and laminar flame speeds in premixed situations of $\text{CH}_4/\text{C}_2\text{H}_4/\text{N}_2$ mixtures. These data, together with numerical simulations with selected kinetic schemes, facilitate our understanding of the low- to intermediate-temperature ignition chemistry and high-temperature flame chemistry of ethylene enriched methane. Computational analysis was then performed to identify the controlling species and elementary reactions in ignition and examine how the oxidation pathways shift with the relative fuel concentrations.

Our second objective was to scrutinize how well the hierarchical requirement of reaction mechanisms is preserved. Specifically, it is recognized that recently there has been substantial interest in the development of reaction mechanisms for hydrocarbon fuels. However, most of these developments have targeted on individual fuels, such as methane, ethylene, propane, etc. Furthermore, while the mechanism of a larger fuel such as ethylene is built upon that of a smaller fuel, such as methane, during the process of mechanism development many of the rate constants are modified in order to achieve agreement with experimental data. As such, the hierarchical requirement of hydrocarbon oxidation kinetics, in that the reaction mechanism of a larger hydrocarbon must degenerate to that of a smaller one, is compromised. The present study therefore represents the first step in a systematic study of fuel hierarchy in mechanism development, by considering the degeneracy to the smallest hydrocarbon, methane, from the next largest hydrocarbon that has a distinctively different molecular structure and reactivity, ethylene. Such a scrutiny can be meaningfully conducted because mechanisms now exist were developed to be chemically descriptive of C1 to C3 hydrocarbons. The fidelity of these mechanisms will thus be tested through experimentation and computation. Further insight into this issue has also been gained by analyzing the reduced mechanisms of the pure fuels and their mixtures.

2. Ignition temperatures in nonpremixed counterflow

2.1 Experiment and computation

The ignition temperatures of N_2 -diluted $\text{CH}_4/\text{C}_2\text{H}_4$ mixtures were measured in a variable-pressure counterflow facility. The components of the apparatus and the experimental methodology were described in detail elsewhere [1]. The method employed for the numerical simulation of ignition was described in Ref.13. The primary chemical kinetic mechanism adopted in this work is a comprehensive C1 to C3 mechanism [14], consisting of 75 species and 529 elementary reactions. An earlier version of this mechanism [15], with 70 species and 463 elementary reactions, was also used for comparison.

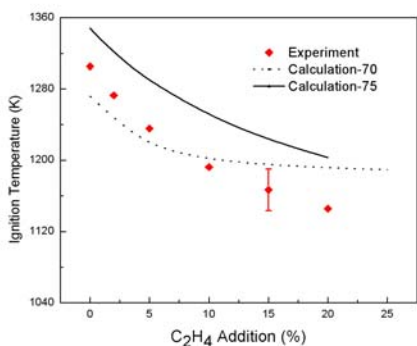


Figure 1: Ignition temperature as a function of C_2H_4 addition, at $p=1\text{atm}$, $k=300\text{ S}^{-1}$

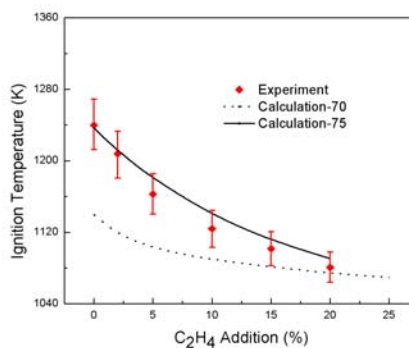


Figure 2: Ignition temperature as a function of C_2H_4 addition, at $p=3\text{atm}$, $k=300\text{ S}^{-1}$

Ignition temperatures were measured with ethylene added to nitrogen-diluted methane, with the mole fraction of methane fixed, as shown in Figs. 1 and 2 for $p = 1$ and 3 atmospheres respectively. The computed results with the two mechanisms are also plotted in the above figures. It is seen that the ignition temperature decreases by about 150 K with 20% ethylene addition, thereby demonstrating that a moderately small amount of ethylene addition to methane indeed promotes methane ignition. It is also of interest to note that while the 75-species mechanism agrees closely with the experimental data at 3 atm, the situation is less clear at 1 atm. That is, while the 70-species mechanism agrees better with the experimental data for low levels of ethylene addition, the enhancement levels off for additions above 10%. On the other hand, although the 75-species mechanism consistently yields higher ignition temperatures than the experiment, the progressive decreasing trend with increasing ethylene addition agrees well with the experiment. Indeed, this trend of early leveling is also exhibited for the computed 3 atm result, which is contrary to the experiment. Thus, in balance, the 75-species mechanism is more descriptive, and as such will be used in the following computational analysis.

2.1 Dominant ignition chemistry

To understand the dominant ignition chemistry, sensitivity and CSP [16-17] analyses were employed. In CSP, chemical reactions are grouped into "modes" based on their characteristic time scales. For ignition problems, the most interesting active mode is the "explosive" mode, which represents a positive eigenvalue group of reactions responsible for the radical growth in time. The structure of this explosive mode at the time when it becomes dominant over the other modes provides the information needed to identify the relevant species and elementary reactions at ignition, through the "radical pointer", "important index" and "participation index". Furthermore, contributions from kinetic and thermal feedback can be quantitatively compared.

CSP was conducted at the location where the time scale of the explosive mode is the shortest, indicating the propensity for the ignition. Figure 3 lists the controlling elementary reactions with large participation index at the ignition state for different mixture compositions. Sensitivity analysis shows largely similar results in identifying the controlling reactions. Together with the information provided by the important indexes, the major oxidation pathway based on the present kinetic mechanism can be summarized by a chemical chart shown in Fig.4. Contributions from CH_4 - and C_2H_4 -leading pathways are determined by the relative fuel concentrations.

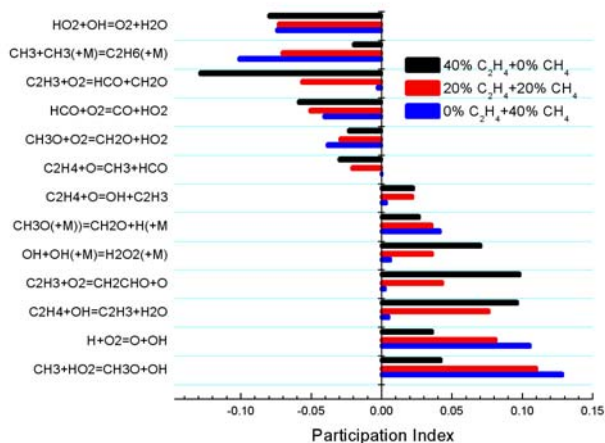


Figure 3: Participation index of explosive modes at ignition states of different mixture composition, $p=1\text{atm}$ and $k=300\text{ S}^{-1}$

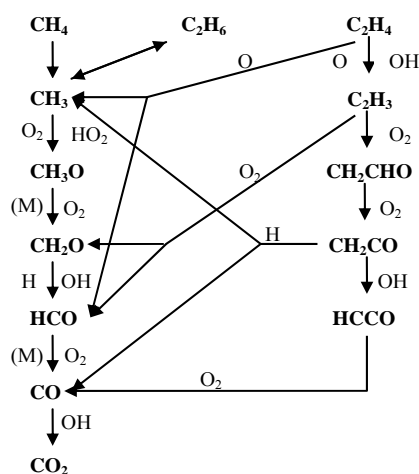


Figure 4: Low-temperature reaction-path diagram for oxidation of $\text{CH}_4/\text{C}_2\text{H}_4$ mixtures

The role of ethylene addition in facilitating ignition is now clear. CH₄ is difficult to ignite because of its high C-H bond energy and the scavenging of the H radical through the initiation step CH₄+H→CH₃+H₂. Furthermore, CH₂O is a slowly reacting radical, which is subjected to the convective and diffusive loss out of the ignition kernel. It is therefore the bottle-neck of the ignition process in a diffusive system. However, in C₂H₄, the C-H bond is easier to break, generating H and C₂H₃ radicals. Second, in addition to the CH₂O pathway, ethylene also provides an additional pathway through CH₂CHO→CH₂CO→HCCO→CO such that the oxidation rate is speeded up. Finally, in addition to the kinetic facilitation, elementary reactions involving C₂H₄ are more exothermic. CSP analysis showed that the ratio of thermal to kinetic contribution to ignition is 0.4 for 40% CH₄ in N₂ and 4.5 for 40% C₂H₄ in N₂, under atmospheric pressure and a strain rate of 300 S⁻¹. Thus when ethylene is added, the thermal feedback becomes progressively stronger and thereby further enhances the ignitability.

3. Laminar flame speeds

The counterflow twin flame technique for the determination of laminar flame speeds is well documented, see, e.g. Refs. 18 and 19. Experiments were conducted at room temperature for mixtures of CH₄ and C₂H₄, from lean to rich, under atmospheric pressure. The data were linearly extrapolated to zero stretch rates to yield the stretch-corrected flame speeds. Numerical simulation was performed by using the one-dimensional flame code [20], allowing for thermal diffusion. The 75-species mechanism was used and the results are compared with the experimentally determined values, as shown in Fig. 5-7.

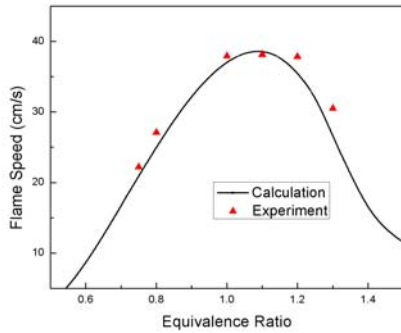


Figure 5: Flame speeds as a function of equivalence ratio, for mixing fraction 0.05

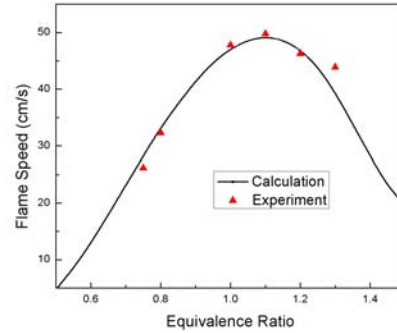


Figure 6: Flame speeds as a function of equivalence ratio, for mixing fraction 0.3

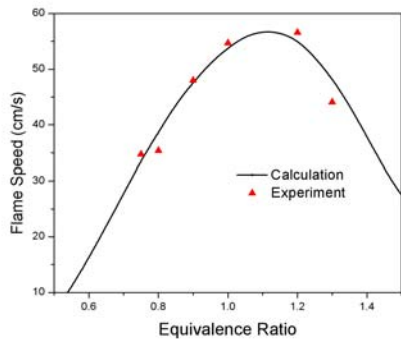


Figure 7: Flame speeds as a function of equivalence ratio, for mixing fraction 0.5

In the above figures, the “mixing fraction”, which is defined in Eqs.1, is fixed. The mixing fraction is a measure of the relative fuel concentrations, weighted by their equivalence ratios respectively.

$$\alpha = \frac{3X_{ethylene}}{3X_{ethylene} + 2X_{methane}} \quad (1)$$

The simulation generally yields good agreement with the experimental data, which demonstrates the accuracy of the high-temperature chemistry of the reaction mechanism. For fixing equivalence

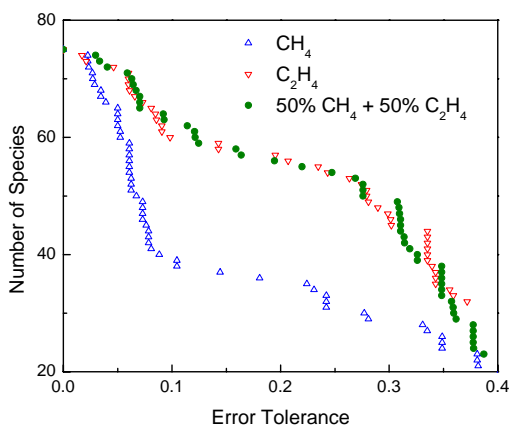


Figure 8: Dependence of number of species in skeletal mechanisms derived by DRG on the user specified error tolerance for pure methane, ethylene, and fuel mixtures. The reduction was based on sampled reaction states from PSR and auto-ignition under 1 atm with equivalence ratio from 0.5 to 1.5. The inlet temperature for PSR is 300K and initial temperature for auto-ignition is from 1000 to 1600K.

skeletal mechanism for the mixture is only slightly larger than that of ethylene for the 10% threshold error. Therefore, based on the present detailed mechanism, the complexity of fuel mixture kinetics is primarily determined by the ethylene chemistry, and the methane kinetics is mostly a subcomponent of that for ethylene. It further supports the argument for the hierarchical structure of detailed kinetics, which requires correct and trustable subcomponents of small molecule kinetics to obtain more complex models for large fuels.

5. Concluding Remarks

CH₄/C₂H₄ mixtures were studied experimentally and computationally with the interests in effects of ethylene addition. Both the ignition temperature and laminar flame speed respond steadily to ethylene addition. The 75-species mechanism yields good agreement with experiments for both cases. The controlling chemistry and major pathways in ignition was identified with sensitivity and CSP analyses. The hierarchical structure of the detailed mechanism was tested by comparison with experiments, and was further assessed by studies on mechanism reduction.

Acknowledgments

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ratio, the flame speed increases gradually and monotonically as ethylene is added to the mixtures.

4. Hierarchical nature of kinetic mechanisms

The kinetics for fuel mixture was further analyzed through mechanism reduction. The important species and reaction pathways that are strongly coupled to the major species such as the fuel were identified by using the method of directed relation graph (DRG) [21-23]. The number of species as a function of the user-specified reduction error is shown in Fig. 8 for pure CH₄, C₂H₄ and a 50-50% mixture respectively. It is seen that the reduction curve for pure methane features a dramatic slope near the threshold error of 0.1, indicating the large extent of reduction with only a minor accuracy loss. The reduction for pure ethylene is more moderate, with a reduction of less than 20 species with about 10% error. The reduction curve for the mixture with 50% methane and 50% ethylene tightly follows that of ethylene, and the

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