

The Chemical Structure of Methane/Air Diffusion Flames:
Concentrations and Production Rates of Intermediate Hydrocarbons.

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INTRODUCTION:

The production of intermediate and large hydrocarbon species is common to most combustion systems. These products range in size from acetylene, benzene and polynuclear aromatic hydrocarbons (PAH) to very large soot particles. Radiation from particles is the dominant mode of heat transfer in large fires. In addition, sampled particles often have PAH adsorbed onto them. Many of these molecules are known carcinogens and their presence on inhalable soot particles poses an obvious long-term health hazard. Despite the important role that such species play in flames and the danger they present as combustion byproducts, the mechanism for their formation is as yet unknown.

Extensive profile studies have led to a detailed understanding of the chemical structure of premixed flames [1]. This information has been combined with the time-temperature history in these one-dimensional systems to produce simple models for the condensation chemistry of premixed flames. Modelling efforts have also been undertaken in shock tubes, although the data set available as input has generally been less extensive [2,3]. Despite the significant progress towards an understanding of soot formation which has resulted from these studies, most practical combustion devices are diffusion flames, and chemical structure data for these environments has only recently been available. Workers in this [4] and other [5] laboratories have recently reported concentration measurements for molecular species, including intermediate hydrocarbons, in laminar diffusion flames. Our work has shown that a knowledge of the local chemical composition alone is not sufficient to predict the concentrations of PAH and soot. We have therefore also collected profile data for temperature and convective velocity in our flame system. In this paper, results for the chemical structure of a methane/air diffusion flame are reviewed. Species concentrations are combined with profiles of velocity and temperature to calculate production rates for intermediate hydrocarbons. The relevance of these calculations to an understanding of soot formation chemistry is discussed.

EXPERIMENTAL APPROACH:

The experimental system has been described in detail elsewhere [4], and will be discussed only briefly below. Laminar methane/air diffusion flames were burned at atmospheric pressure on a Wolfhard-Parker slot burner. Fuel exits a central 8mm wide slot and air flows through two 16mm wide adjacent slots. Thus, two flame sheets are formed near the fuel/air interfaces, which are symmetric about the burner centerline. The flame is stabilized by wire screen "gulls" located 45mm above the burner surface. Concentration profiles of numerous stable flame species were collected via a direct-sampling mass spectrometer equipped with a quartz microprobe [6]. Calibrations were performed by measuring the signal for a particular molecule sampled from a mixture of known composition of the species with argon at room temperature. Calibration factors were then corrected for the variation of the mass flow through the sampling orifice as a function of temperature. For species which could not be calibrated directly, factors for similar species were adjusted by multiplying by the ratio of their respective ionization cross-sections.

Temperature profiles were measured with an uncoated fine wire Pt/Pt-10%Rh thermocouple. Corrections due to radiation effects are less than 7% at the highest temperatures in this flame [4], while catalytic effects are expected to be small [7] and in the opposite direction. Horizontal and vertical components of the convective velocity were determined using laser Doppler velocimetry. These measurements were made by seeding the flow with nominal 1 μ m diameter aluminum oxide particles. The temperature and velocity profiles were obtained at heights ranging from near the burner surface to 20 mm above the burner. Mass spectrometric measurements were limited to a minimum height of 3 mm above the burner (due to the 6mm diameter of the microprobe) and a maximum height of 15 mm above the burner. Above 15 mm, clogging of the probe orifice by soot particles was observed and quantitative sampling was no longer possible. The gradients in concentration and temperature in this flame are steepest in the horizontal direction. Therefore, profile data points were collected every 0.2 mm in the lateral direction and every 2 mm in the vertical direction.

RESULTS:

Figure 1 illustrates the temperature and velocity fields for this flame. Shown in solid lines are isothermal contours determined from the thermocouple profiles. Note the bowing out of the flame along the 1900 K contour away from the slot separators located at ± 4 mm with respect to the burner centerline. Also shown are streamlines of convective velocity calculated from the two measured velocity components. The streamlines exhibit trajectories which begin in the lean region of the flame, cross the high temperature reaction zones, and continue into the fuel-rich regions.

Figure 2 shows mass-spectrometric profiles of the concentrations of a variety of stable flame species at a height of 9 mm above the burner. A number of points are noteworthy in comparing

Figures 1 and 2. First, the concentrations of oxygen and methane disappear near the high temperature reaction zone at ± 6 mm from the burner centerline, where the concentration of water is at a maximum. Second, the high concentration of nitrogen near the burner centerline reveals that significant entrainment of air (as shown by the velocity measurements in Fig. 1) and diffusion of nitrogen toward the burner centerline occur. Also shown in Fig. 2 is a summation of mole fractions for all species present in the flame at a concentration of 1% or greater. The close agreement to an ideal mass balance of 1 throughout the flame is a measure of the success of our calibration scheme.

Figure 3 illustrates profiles collected at 9mm above the burner surface for a variety of intermediate hydrocarbons: acetylene, benzene, diacetylene, and butadiene. Peak concentrations at this height for these species are 6200, 800, 570, and 110 parts per million, respectively. Profiles for a large number of additional intermediate hydrocarbons were obtained, and all have concentration maxima in the same region of the flame.

DATA ANALYSIS

One of the primary goals of our work is the application of kinetic modelling to a methane/ air diffusion flame. The approach we have adopted is to compare the predictions of models which have been used successfully in premixed flames and shock tubes with our experimental results. A successful model must not only account for the steady state concentrations of species involved in the soot formation process, but also for the net rate of reactions for these species in the flame. Therefore, as a first step in the application of detailed kinetic modelling to our flame we have sought to derive the net chemical flux for profiled species from our concentration, temperature and velocity measurements. The procedure for this calculation is described below.

A laminar flame is a steady-state system: the value of any macroscopic variable (such as a species concentration) does not change with time at a particular spatial location [6]. Because there is a flux into and out of a given volume element due to mass transport, there must be a corresponding change in the species concentration due to chemical reactions:

$$R_i = \nabla [N_i (v + V_i)] \quad 1)$$

Here, R_i is the net chemical rate, N_i is the species concentration, v is the mass average (convective) velocity, and V_i is the diffusion velocity of the species into the local mixture. This diffusion velocity can be calculated by first computing the effective diffusion coefficient, $D_{i,mix}$, where contributions from all species present in the flame with a concentration greater than 1% are included:

$$V_i = - \frac{D_{i,mix}}{x_i} \cdot \nabla x_i \quad 2)$$

Figure 4 illustrates this calculation for acetylene production rates at a height of 9mm above the burner. Contributions from the convective and diffusive velocities to the net chemical rates are shown. Note the strong diffusive velocity away from the burner centerline into the high temperature reaction zone, where acetylene is oxidized. Figure 5 indicates that the chemical role of acetylene changes with height above the burner. Low in the flame the destruction rate exhibits a maximum value ($R_i = -1.0 \times 10^{19}$ molecules/(cc·sec)) near the high temperature, primary reaction zone, and the production rate feature ($R_i = 1.5 \times 10^{19}$ molecules/(cc·sec)) occurs slightly toward the fuel side. This peak in the production rate is located on the high temperature side of the observed maximum in the concentration profile (see Fig. 3). Higher in this flame it appears that the production rate peak is diminished by a new destruction feature (see arrow in Figure 5). An additional loss mechanism for acetylene higher in the flame is consistent with the proposed importance of this intermediate hydrocarbon in particle growth chemistry. The location of this new feature coincides with the peak concentrations of very small soot particles detected in our earlier work [4].

CONCLUSIONS AND FUTURE DIRECTIONS:

We have made quantitative species concentration measurements and analyzed these profile data to obtain chemical rates for production and destruction of intermediate hydrocarbons in a methane/air flame. In the near future detailed kinetic models will be evaluated at specific flame locations in an attempt to verify their application to diffusion flame systems. Specifically, can the models (given as inputs measured concentrations, temperature, and mass transport) predict net chemical fluxes which agree with our measured production rates? An analysis such as this will indicate possible shortcomings in both our knowledge of the chemical structure of these systems (i.e., radical concentrations are not well known) as well as deficiencies in proposed models for chemical growth.

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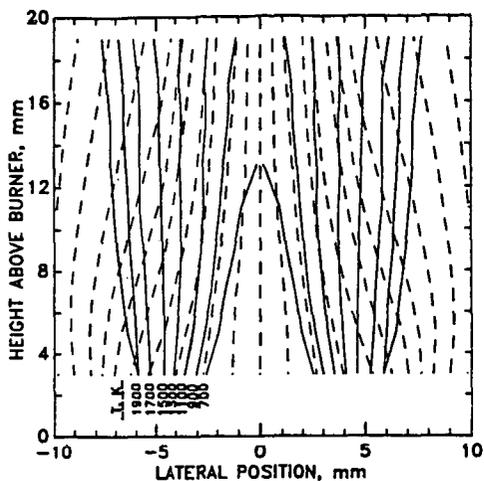


Figure 1: Isothermal contours (solid lines) calculated from uncorrected thermocouple measurements and streamlines (dashed lines) calculated from the velocity measurements for the methane/air flame.

Figure 2: Mass spectrometric measurements of some of the major species. The N_2 profile has not been corrected for the small amount of CO detected at the same mass. At the top of the figure the sum of the mole fractions of all of the species present in the flame at a concentration of 1% or greater is shown. The dashed line represents the average value of 1.01 ± 0.04 .

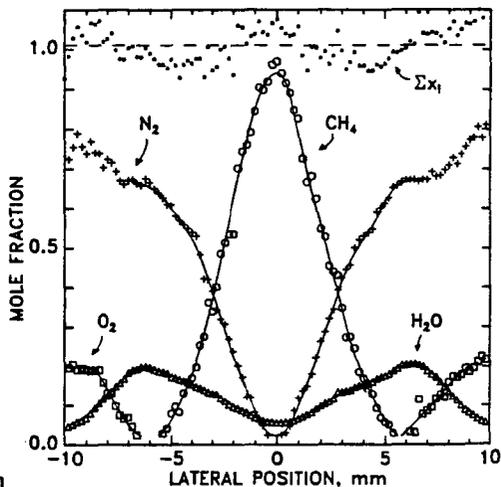
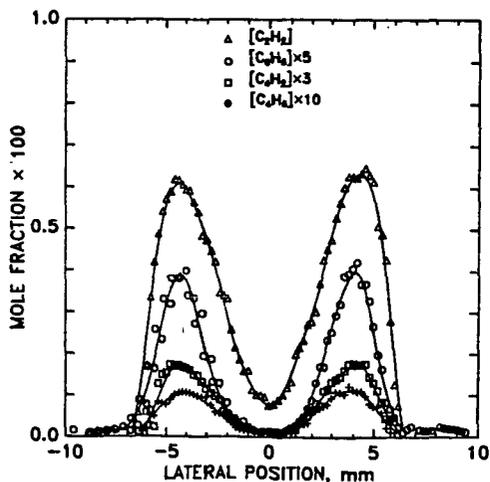


Figure 3: Mass spectrometric profile measurements of several minor species: acetylene, benzene, diacetylene, and butadiene at a height of 9mm above the burner.



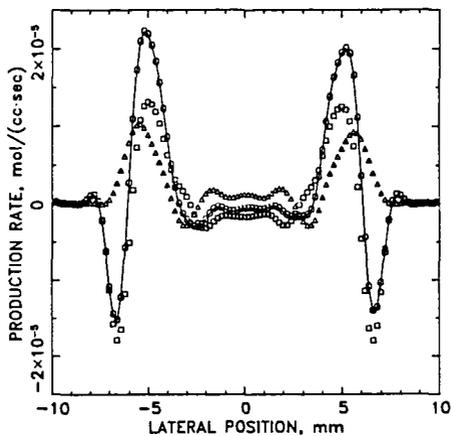


Figure 4: Contributions to the net chemical production rate (the connected circles) from diffusive (squares) and convective (the triangles) terms in Eq. 1 at 9mm above the burner.

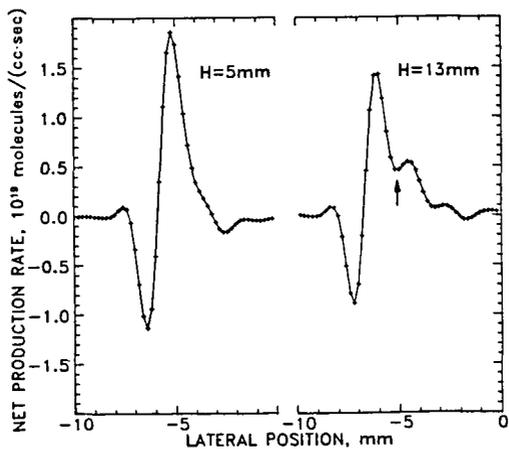


Figure 5: Profiles of the net chemical production rate for acetylene at two heights in the flame; only the left hand side of the flame is shown.