Soot Inception in a Methane/Air Diffusion Flame as Characterized by Detailed Species Profiles

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Detailed species concentration profiles have been measured using optical and mass spectrometric methods in an atmospheric pressure methane/air diffusion flame burning on a Wolfhard-Parker slot burner. Relative concentrations have been determined for OH by laser-induced fluorescence and, in addition, laser-induced production of C_2 has been monitored by fluorescence measurements. Broadband ultraviolet and visible fluorescence have been observed, and both are attributed to PAH, although other molecules may be responsible for these emissions at elevated temperatures. Small soot particles were detected by laser-induced ionization. Using a direct sampling mass spectrometer, absolute concentrations have been measurements of several additional intermediate hydrocarbons have also been made, including methylacetylene (and/or allene), vinylacetylene, diacetylene, triacetylene, benzene, and naphthalene.

These profiles are combined with velocity, temperature, and Rayleigh scattering measurements to characterize the region of chemical growth in a luminous diffusion flame. The soot inception zone occurs at the high temperature edge of a region in which intermediate hydrocarbons are abundant. The positions of the peak concentrations for these species follow isothermal contours as a function of height above the burner. This result illustrates the dominant role of chemical steps in the growth processes which lead to the formation of the earliest soot particles. An analysis of the species concentration profiles in terms of the local equivalence ratio successfully correlates the data for the major species and the temperature, but is not adequate for any of the profiles of the intermediate hydrocarbons or for the small soot particles.

I. INTRODUCTION

In a hydrocarbon diffusion flame, soot formation occurs by a series of chemical steps which involve initial pyrolysis reactions, i.e., the breakdown of the parent fuel molecule, followed by condensation reactions which lead to chemical growth. Numerous proposals have been advanced concerning the important buildup processes [1-4], but the detailed mechanism has not yet been elucidated. The focus of this paper is the measurement of species profiles for intermediate hydrocarbon molecules such as acetylene, benzene, and polycyclic aromatic compounds, in a luminous methane/air diffusion flame. Both laser-based optical techniques and direct-sampling mass spectrometric methods have been used and combined to give new information on the chemical structure of this flame. The aim of our work is to improve the understanding of soot formation processes, specifically the early chemical steps which lead to the formation of larger molecules and eventually to particle inception.

Optical measurements are well suited for diffusion flame investigations, since high spatial

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resolution is required because of the steep concentration and temperature gradients. Most optical studies in recent years have concentrated on characterizing the soot particle field in terms of the soot volume fraction, particle size, and number density [5-14]. Detailed profile measurements have yielded considerable information on the growth of soot particles but little data on the early chemical steps which produce the first particles. Several earlier investigations in diffusion flames have reported the detection of intermediate hydrocarbon species by laser-induced broadband fluorescence, usually in the visible region [6-8, 12, 13, 15, 16]. These spectra have been attributed by some workers [in particular, 13, 15] to polycyclic aromatic hydrocarbons (PAH), which have often been proposed as important precursors and perhaps building blocks in models of soot formation [2]. The present results extend these measurements: profiles of both ultraviolet and visible laserinduced broadband fluorescence have been obtained. Three distinct contributions, all tentatively assigned as PAH fluorescence, are observed. In addition, profiles have been measured for the fluorescence from OH and C₂ radicals and for the laser-induced ionization of very small soot particles. The C₂ radicals were produced by laser photolysis of one or more larger molecules.

Sampling studies have also been made in a number of hydrocarbon diffusion flames [17-30] using gas chromatography and coupled gas chromatography/mass spectrometry for analysis of stable species. The products of both the fuel decomposition and subsequent condensation reactions giving larger molecules have been detected. In some cases, most notably the work of Kern and Spengler [21, 22] and Prado et al. [28], aromatic compounds have been observed. The present measurements have been carried out in a methane/air diffusion flame at atmospheric pressure using a direct-sampling mass spectrometer. Absolute concentrations of methane, acetylene, butadiene, and toluene as well as hydrogen, nitrogen, oxygen, carbon dioxide, and water have been determined using a direct calibration procedure. In addition, measurements are reported for methylacetylene (and/or allene), vinylacetylene, diacetylene, triacetylene, benzene, and naphthalene, for which an indirect calibration method was employed.

These optical and mass spectrometric species profiles have been combined with laser Doppler velocimetry measurements to characterize the velocity field and thermocouple determinations of the temperature field. Together these data provide a more complete description of the chemical structure in a diffusion flame than has been available previously, with particular emphasis on intermediate hydrocarbon molecules which are likely to be involved in chemical growth processes which lead to larger species. The soot inception region is found to occur at the high temperature edge of a zone which is rich in intermediate hydrocarbon combustion products. The peak concentrations of these intermediate species and of the small soot particles follow isothermal temperature contours well to the fuel side of the region of maximum temperature. Detailed species profiles such as those presented here provide some of the information which is needed for identifying the probable chemical routes to soot formation in diffusion flames.

II. EXPERIMENTAL APPROACHES

A. Wolfhard-Parker Slot Burner

Methane/air diffusion flames were burned at atmospheric pressure on an open Wolfhard-Parker slot burner [10,31], shown in Fig. 1. Fuel flows through an 8 mm \times 41 mm center slot and oxidant (air) through two 16 mm \times 41 mm slots, thus creating two flame fronts. In order to obtain uniform flow conditions, the burner chambers were filled with 1 mm diameter glass beads which were covered by copper screening at \sim 3-4 mm below the burner surface. A rectangular, wire screen chimney with "gulls," similar to that described by Kent et al. [10], was used to stabilize the flame. These gulls anchored the flame at a height of 45 mm, and measurements were carried out from 1 to 21 mm



Fig. 1. Schematic diagram of the Wolfhard-Parker slot burner and the optical setup for fluorescence measurements. P is the polarizing filter, and L1 and L2 are the focusing and collecting lenses, respectively. The flame was stabilized by two curved screens and enclosed by a rectangular chimney made of the same material.

above the burner surface. Repeat measurements gave reproducible results. Temperature, velocity, and species profiles were obtained by moving the burner in the lateral direction (along the x-axis in Fig. 1) at a series of heights, using a programmable micrometer stage. The laser and detection optics or the mass spectrometer sampling probe remained fixed. The cold flow velocity of the air was twice that of the fuel, typical values being 19.4 and 9.7 cm/s, respectively. For these conditions the total flame height was ~ 300 mm, and no soot was emitted at the tip. Chemically pure (\geq 99 mole percent) methane was used for all measurements.

B. Temperature and Velocity Measurements

Temperature profiles were obtained using uncoated 125 μ m diameter Pt/Pt-10% Rh fine wire thermocouples. The butt welded junction was somewhat larger than the thermocouple leads; microscope photographs showed the bead to be approximately 180 μ m in diameter. The thermocouple wires were mounted on 250 μ m diameter supports. In the temperature data no evidence was found for effects due to soot coating of the thermocouple; the profiles were smooth (no discontinuous jumps) and symmetric about the center of the burner. Only when the thermocouple supports were located in the high temperature flame zones did conduction effects cause erroneously high values to be recorded for temperatures in one of the air streams (see Fig. 2 in the Results Section).

All of the temperature data are reported as uncorrected thermocouple values. An estimate of the radiation correction can be obtained by assuming that a steady state exists between convective heat transfer to and radiation from the thermocouple. This approach neglects conduction effects along the thermocouple leads and radiative heat transfer from the surrounding gas to the thermocouple. A simple relationship can then be given for the temperature correction, ΔT ,

$$\Delta T = \frac{\sigma \cdot \epsilon \cdot d}{\mathrm{Nu} \cdot k} \cdot (T_{\mathrm{TC}}^{4} - T_{\mathrm{b}}^{4}), \qquad (1)$$

where σ is the Stefan-Boltzmann constant, ϵ is the thermocouple emissivity, d is the appropriate diameter, Nu is the Nusselt number, k is the gas conductivity, $T_{\rm TC}$ is the thermocouple temperature, and $T_{\rm b}$ is the background temperature. Values for ϵ and k are readily available [32, 33]. The major difficulty in the analysis concerns the appropriate selection of the Nusselt number. Estimates of Nu can be obtained as a function of the Reynolds number for the flow around the thermocouple [33]. For a typical flow velocity in our flame of 60 cm/s, values of Nu vary between 0.5 and 1.0 for a cylindrical wire and 2.0 and 2.2 for a spherical bead. Since ΔT varies inversely with Nu, the choice between the cylindrical wire and the spherical bead approximation is critical. Based on the microscope photographs of the thermocouple junction, a spherical geometry has been assumed in order to estimate the radiation correction. Table I lists the calculated corrections for several temperatures characteristic of the methane/air diffusion flame; ΔT is significant only in the regions of highest temperature.

TABLE I

Radiation Corrections for the Thermocouple Measurements Assuming a Spherical Bead Geometry

Thermocouple Temperature (K)	Emissivity ^a	Radiation Correction (K)
1300	0.186	+ 31
1500	0.205	+ 54
1700	0.223	+ 87
1900	0.236	+ 129

^a Values taken from D. Bradley and A. G. Entwistle [32]. The gas conductivity values were taken to be that of air [33].

Velocity profiles were measured by laser Doppler velocimetry, using nominal 1 μ m diameter aluminum oxide particles to seed the methane and air flows. Both the vertical and horizontal components were determined. The laser velocimeter was a conventional dual beam system in which the incident beam from an argon ion laser (typical power ~ 1 W) was split into two parallel beams of equal intensity. These beams were then focused and crossed to form a probe volume with a diameter of 0.16 mm and a length of 1.7 mm. Light scattered in the forward direction from the probe volume was collected with a lens and focused onto a photomultiplier tube. The resulting signals were then analyzed using a burst signal processor to obtain the velocity. For the horizontal velocity component, a Bragg cell was used to impart a 40 MHz frequency shift to one of the two beams which formed the probe volume. This frequency shifting approach provides a means for determining both the direction and the magnitude of the velocity. In addition, the frequency offset at zero velocity is useful when the magnitude of the velocity component is small.

C. Optical Measurements

Two different laser systems were used in making the species profile measurements. A continuous-wave argon ion laser operating with an output power of 1.3 W at 488 nm was utilized for Rayleigh scattering measurements and the excitation of broadband visible fluorescence. For the remaining profiles a pulsed Nd:YAGpumped tunable dye laser, whose output beam could be frequency doubled into the near-uv spectral region, was employed. Typical output energies were 1-2 mJ/pulse in the uv beam and 3-30 mJ/pulse for visible laser excitation. In all of the optical measurements the laser beam irradiated the flame parallel to the burner slots, and fluorescence and scattering were observed at 90° with respect to the beam. Figure 1 shows the optical setup. The incoming laser beam was focused with a 300 mm focal length lens for all of the scattering and fluorescence profiles except in the case of the excitation of ultraviolet broadband fluorescence. For these measurements no focusing lens was used, and the spatial resolution of the profile was determined by collimation of the incident beam using two irises to give a beam diameter of ~ 1 mm. Laserinduced scattering and fluorescence were detected using a 0.35 m grating monochromator with a bandpass of 0.4-1.2 nm. For the profiles obtained with the argon ion laser, the incoming beam was vertically polarized, and so a polarization filter placed in front of the monochromator slit was used to detect preferentially either the depolarized visible fluorescence (inelastic scattering) or the highly polarized Rayleigh scattering and scattering from soot particles (elastic scattering).

The laser-induced fluorescence experiments were carried out as follows: OH was excited near 282 nm in the (1, 0) band of the $A^2\Sigma^+ - X^2\Pi$ electronic system and detected at 308.9 nm in the (0, 0) band. C₂ was excited at the (0, 1) bandhead of the Swan system, $d^3\Pi_g - a^3\Pi_u$, at 563 nm, and detected in the (0, 0) band, at 516.5 nm. Broadband fluorescence was studied in the visible and ultraviolet regions, the former excited at 488 nm and detected at 510 nm and the latter excited at 282 nm and observed at 345 nm.

For the C_2 profile measurements the laser intensity was sufficiently high (20-30 mJ/pulse focused with a 300 mm lens) that photolytic decomposition of larger species readily occurred. This photolysis was investigated in experiments using two lasers-a high intensity pump beam and a weak probe beam. The probe beam detected any C2 present, either nascent C2 produced in the flame or laser-produced C2. Our results showed that C2 was readily formed by the high intensity pump beam in the 560-575 nm wavelength region and that the concentration of nascent C2 was very small compared with laserinduced C₂ production. For the high laser intensities used in the profile measurements the Swan system of C_2 is optically saturated [34], yet removing the focusing lens for the incoming laser beam reduced the fluorescence signal by more than 95%. This indicates that most of the observed C₂ fluorescence was due to laserinduced production of C2. Additional experi-

ments in which the laser intensity was varied showed that the C_2 production process was not optically saturated; the fluorescence signal varied strongly with the laser intensity, suggesting a multiphoton excitation process to yield C₂. In marked contrast the OH fluorescence signal was reduced only about 20% when the focusing lens for the excitation beam was removed. For the OH experiments the laser intensity was about 10 times less than that used in the C2 profile measurements, and OH has a smaller oscillator strength for the A-X system than does C_2 for the Swan system [35]. Based on these OH observations, a significant concentration of nascent C₂ should have been readily observable using unfocused laser irradiation.

Previous work at high laser intensities has shown that photodecomposition of large soot particles can produce C_2 [36–38]. However, in our methane/air diffusion flame the concentration of large particles was negligible at lower heights, and the earliest, small soot particles were not observable by elastic scattering until a height of 15 mm above the burner was reached. In contrast, laser-produced C_2 was observed even at 1 mm above the burner. Thus, the present detection of C_2 production must be due to the photolysis of molecular species rather than soot particles. This measurement therefore helps to identify the region wherein molecular growth chemistry is occurring.

In some experiments laser-induced ionization was detected by inserting a 1 mm diameter tungsten electrode into the flame perpendicular to and just above the laser beam. This electrode was typically biased at -800 V, and the burner body provided the ground return. Electrons created during the ionization process induce a current in the circuit as they move toward the grounded burner. The presence of the electrode was observed to have no effect on the OH fluorescence measurements and is thus thought not to perturb the flame at the location of the laser beam. In the present experiments visible light from the pulsed Nd: YAG-pumped tunable dye laser in the 555-580 nm region produced wavelength independent ionization signals which are attributed to the multiphoton ioniza-

tion of small soot particles. A 100 mm focal length lens was used in these measurements. Similar studies made in our laboratory on premixed flames have determined that the mass range of the species ionized under those conditions was 2300-6100 amu, corresponding to spherical particles of diameter 1.8-2.2 nm [39]. Those premixed flame results were obtained from a mobility analysis in the downstream region of a rich acetylene/air flame. For the methane/air diffusion flame investigated here, similar mesurements are difficult to make due to the steep temperature and concentration gradients. Nevertheless, a comparison of arrival time data for the laser-produced positive ions reaching the electrode gave consistent results for the diffusion and premixed flame conditions. This suggests that the same size small soot particles were ionized in the profiles presented in the Results Section.

D. Mass Spectrometric Measurements

Samples were withdrawn from the methane/air diffusion flame using a quartz microprobe, which was designed from the description given by Fristrom and Westenberg [40]. A 6 mm o.d. quartz tube was tapered to a tip with an orifice diameter of ~140 μ m. This tube was inserted into the center of the flame and aligned parallel to the burner slots in order to minimize pyrolysis of the sampled gases inside the probe. The pressure downstream from the probe was typically 13-40 Pa (0.1-0.3 Torr) during the profile measurements. Gas was sampled from this intermediate pressure region with another quartz microprobe and then passed directly into the ionizer region of a quadrupole mass spectrometer. Typically, the mass spectrometer was operated in the single mass mode, and the output from the ion multiplier was digitized and stored in a computer. The electron energy was set at 20 eV in order to minimize molecular fragmentation.

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. Thus,

effects due to mass bias in the orifice, ionization efficiency, mass-filter throughput, and ion detection efficiency could be eliminated. Calibrations of this sort were performed for H_2 , CO_2 , N_2 , O_2 , CH_4 , C_2H_2 , C_4H_6 , and C_7H_8 . Water was calibrated against the relative humidity measured in the room air. For uncalibrated species (including C_4H_2 , C_6H_6 , and $C_{10}H_8$) approximate calibration factors were estimated from the ratio of their ionization cross sections at 75 eV to those of similar species which could be directly calibrated. The electron impact ionization cross section at 75 eV for a hydrocarbon molecule can be estimated by summing atomic contributions [41]. If similar species are compared which have nearly equal ionization potentials, such as benzene and toluene, then the ratio of their ionization cross sections at 20 eV can be taken to be the same as that at 75 eV [42].

In order to make quantitative mass spectrometric measurements, it is assumed that the observed signal intensity, S_i , is proportional to the molecular flow rate, \dot{N}_i , through the orifice in the sampling probe:

$$S_{i} \propto \dot{N}_{i} = \dot{m}_{i} \cdot (N_{0}/M), \qquad (2)$$

where \dot{m}_i is the mass flow rate, M is the molecular weight of the species sampled, and N_0 is Avogadro's number. The mass flow rate through a critical flow orifice for a pure gas is given by [40]

$$\dot{m}_{\rm i} = C \cdot a \cdot \frac{\rho_{\rm i}}{N_0} \cdot ({\rm MRT} \cdot F)^{1/2}, \qquad (3)$$

where

$$F = \gamma \cdot \left[\frac{2}{\gamma+1}\right]^{(\gamma+1)/(\gamma-1)}$$

and C is the discharge coefficient, a is the area of the probe orifice, ρ_i is the number density, and γ is the heat capacity ratio. For polyatomic molecules F changes by less than 5% between 300 and 1500K; F, C, and a were all taken to be independent of temperature. For a mixture of gases, the total mass flow rate was assumed to be the sum of the individual mass flow rates. This implies that the mass flow rate of a specific species is independent of the composition of the bulk fluid. Acetylene signals in mixtures with methane and argon (5% acetylene, 95% diluent) were compared and were found to be essentially identical, thereby justifying this assumption.

Collecting constants in Eqs. (2) and (3) into k_i , the observed signal intensity is found to depend on the species number density in the sampled volume and on the temperature of the sampled gas:

$$S_i = k_i \cdot \rho_{i,T} \cdot (T)^{1/2}.$$
 (4)

The calibrations of mixtures with known composition were carried out at room temperature; the measured signal is

$$S_{i} = K_{i,300} \cdot \rho_{i,300},$$
 (5)

where $K_{i,300}$ is the calibration factor at 300K. Thus, from Eqs. (4) and (5)

$$K_{i,300} = k_i \cdot (300)^{1/2} \tag{6}$$

and

$$S_{\rm i} = \frac{K_{\rm i,300}}{(300)^{1/2}} \cdot \rho_{\rm i,T} \cdot T^{1/2}, \tag{7}$$

or the species number density is

$$\rho_{i,T} = \frac{S_i}{K_{i,300}} \cdot \left[\frac{300}{T}\right]^{1/2}.$$
 (8)

Profiles were obtained at heights from 3 to 15 mm above the burner surface in 2 mm increments. The lower limit of 3 mm is due to the 6 mm diameter of the quartz tubing, while the upper limit of 15 mm was determined by clogging of the orifice by soot particles in the luminous regions of the flame. At 15 mm above the burner the Rayleigh scattering measurements first show evidence for soot particles. These scattering signals grow rapidly with increasing height.

The approximate spatial resolution of the quartz microprobe was determined from sampling measurements made on argon flowing through a second, similar probe which was positioned along a perpendicular axis. The resulting argon profile was approximately Gaussian in shape, so that an effective sampling diameter of 0.7 mm could be estimated by assuming that the experimental profile represented the convolution of two Gaussian profiles. This value of the sampling diameter corresponds to five orifice diameters [43]. Therefore, for the flame measurements the shape of the sampling volume was taken to be symmetric about the probe orifice.

III. RESULTS

Temperature, velocity, and species profiles were measured across the burner, perpendicular to the fuel and air slots (along the x-axis in Fig. 1), at the center (with respect to the y-axis) of the methane/air diffusion flame. Data were obtained at 2 mm height increments above the burner surface; selected profile measurements are presented below.

A. Temperature and Velocity Measurements

Figure 2 shows thermocouple measurements at three heights above the burner. These profiles reveal that with increasing height the peak temperature regions move away from the centerline and the centerline temperature increases. The temperatures shown have not been corrected for radiation losses, which increase the values by 130K in the zones of highest temperature (see Table I). Thus, these regions are about 150K below the stoichiometric, adiabatic methane/air flame temperature of 2225K calculated using the NASA equilibrium code [44]. The species profile measurements discussed below show that intermediate hydrocarbons produced in condensation reactions appear in a region 3-5 mm from the burner centerline, on the fuel side of the high temperature zones. Here the temperature gradients are steep, 200-250K/mm. From the thermocouple measurements, isothermal contours have been determined and are presented in Fig. 3.

Figure 4 shows profiles of the vertical and horizontal velocity components obtained using laser Doppler velocimetry; measurements were made at heights of 3-19 mm above the burner.



Fig. 2. Thermocouple temperature profiles at heights of 3, 9, and 15 mm above the burner; the data are not corrected for radiation losses (see Table I). At the right-hand side of the figure the temperature values in the air flow are erroneously high due to heating of the thermocouple via conduction along the thermocouple supports.

For the vertical component the peak velocity increases from 58 cm/s at 3 mm to 103 cm/s at 19 mm, while the centerline velocity accelerates from 19 to 82 cm/s over the same region. This strong acceleration leads to significant entrainment from the air streams. The peak value of the horizontal velocity component is 25 cm/s inward toward the fuel zone and remains approximately constant from 3 to 19 mm. Figure 5 presents the streamlines computed from the velocity measurements and shows the resulting convection toward the fuel zone.

Similar velocity measurements have been made on a Wolfhard-Parker burner enclosed by a chimney by Kent et al. [10] and Kent and Wagner [11]. Their results also show rapid acceleration of the vertical velocity component along the centerline, strong entrainment from the air to the fuel side, and buoyant flow conditions. Their horizontal velocity component was calculated to be 20 cm/s low in the flame, and this decreased with height above the burner [11].

Since the methane/air diffusion flame is characterized by large temperature gradients, thermophoretic forces could influence the trajectories of the aluminum oxide seed particles. This effect is small in our experiments. The nominal 1 μ m diameter of the seed particles is approximately equal to the gas mean free path in the region where intermediate hydrocarbons are observed, 3-5 mm from the burner centerline,



Fig. 3. Isothermal contours for the left-hand side of the methane/air diffusion flame; the uncorrected thermocouple data have been used.

and so these particles have a Knudsen number of ~ 1 . This is characteristic of the transition region between the free molecular flow and the continuum flow regimes. Using the analysis appropriate for the free molecular regime to establish an upper limit [45, 46], the thermophoretic velocity is estimated to be ≤ 1.5 cm/ s. This value is only 6% of the peak horizontal velocity component, which occurs 4-5 mm from the burner centerline. Thus, the streamlines computed from the LDV measurements on aluminum oxide particles should accurately represent the gas flow conditions in the methane/air diffusion flame. In the experiments of Kent and Wagner [11] the effect of thermophoresis on the soot particles was also found to be small; they estimated a contribution to the horizontal velocity component of 2 cm/s.

B. Optical Measurements: Laser-Induced Fluorescence

Number density and mole fraction are useful ways in which to present species profile concentrations, either in absolute or relative measurements. Most of the optical profiles reported here were obtained using laser-induced fluorescence. For low intensity excitation in a two-level system the observed fluorescence signal, S, is given by

$$S = cN_1 B_{12} I_{\nu} \cdot \left(\frac{A_{21}}{A_{21} + Q}\right), \qquad (9)$$

where N_1 is the number density of the ground electronic state, B_{12} is the Einstein coefficient for absorption, I_{ν} is the laser intensity, A_{21} is the rate of spontaneous emission, Q is the quench-



Fig. 4. Vertical and horizontal velocity components measured at heights of 3, 9, and 15 mm above the burner.



Fig. 5. Streamlines computed from the velocity measurements at heights from 3 to 19 mm above the burner. Every fifth streamline is shown for the left-hand side of the methane/air diffusion flame.

ing rate of the rovibronic levels of the excited electronic state which are utilized for fluorescence detection, and c is a constant. The steep temperature gradients present in our diffusion flame can have an important effect in determining concentrations, since the quenching rate, Q, depends upon temperature. Under constant pressure conditions

$$Q = \rho \cdot v \cdot \sigma \propto 1/\sqrt{T}, \qquad (10)$$

where ρ is the gas number density, v is the species velocity, and σ is the quenching cross section (assumed to be constant although the gas composition changes across the diffusion flame). Thus, the observed signal intensity for a

constant species number density is also a function of temperature for low intensity optical excitation.

However, for the pulsed laser energies and focusing conditions in our experiments the optical excitation is not low intensity. The optical transitions for the OH, C_2 , and the uv broadband fluorescence measurements are all one-photon allowed, and the pulsed laser intensities easily approach conditions of optical saturation. Following the analysis of Baronavski and Mc-Donald [34], the fluorescence signal is given by

$$S = cN_1 \cdot \left[1 - \frac{A_{21} + Q}{(B_{21} + B_{12}) \cdot I_{\nu}} \right] , \qquad (11)$$

where B_{21} is the Einstein coefficient for stimulated emission. For high laser intensities, therefore, the observed signal is proportional only to the lower state population, since the second term in Eq. (11) becomes small.

The profiles shown in Figs. 6 and 7 are the

original data obtained from the optical measurements. For the OH fluorescence, the uv broadband fluorescence, and the C_2 production, these profiles represent relative concentration measurements. Only for visible broadband fluorescence is quenching likely to be important, since



Fig. 6. Optical profile measurements of OH fluorescence, C_2 fluorescence, and Rayleigh scattering at heights of 3, 9, 15 mm above the burner. The zero positions have been offset for clarity. The C_2 radicals are produced by laser photolysis from an unknown precursor.



Fig. 7. Optical profile measurements of soot ionization, broadband visible fluorescence, and broadband ultraviolet fluorescence at selected heights above the burner. The zero positions have been offset for clarity. Both the visible and ultraviolet fluorescence are attributed to polycyclic aromatic hydrocarbons (PAH); the former was detected at 510 nm, and the latter was monitored at 345 nm.

these profiles were obtained using the low intensity, continuous-wave argon ion laser for optical excitation. Knowing the temperature, this profile can be replotted in terms of relative concentrations if one assumes that the quenching cross section does not vary with the molecular environment. This assumption has not been tested in diffusion flames, and so the visible fluorescence profiles should be interpreted in terms of relative concentrations with some caution.

Figure 6 presents profile measurements for OH fluorescence, C₂ production, and Rayleigh scattering at three heights above the burner. The OH and C₂ profiles are symmetric about the burner centerline, and the OH profile shows no evidence for self-absorption. Several profiles for OH were obtained in which different rotational lines were excited; all showed the same widths and peak positions at a given height. The Rayleigh scattering profiles complement the temperature measurements displayed in Fig. 2. Low in the flame the measured scattered light intensities obtained in the outer region of the air flow and at the centerline of the methane fuel region correspond closely to the known relative Rayleigh scattering cross sections [47]. At a height of 15 mm, small shoulders are discernible at approximately ± 4.8 mm and are attributed to soot particle scattering. These features grow rapidly to become large peaks higher in the flame.

It is of interest to analyze these results by following the spatial position of the peak signal intensity for each profile. For example, the OH peak follows the maximum temperature region, moving away from the centerline with increasing height. However, on the fuel side the OH concentration falls sharply and the peak OH concentration lies just outside the point of highest temperature. Well to the inside of the maximum temperature region the photolytic C_2 production profile occurs; the peak intensity grows by a factor of over 100 from 1 to 21 mm above the burner, and the peak position moves slightly toward the fuel zone.

At a height of several millimeters above the burner, intermediate size hydrocarbons are

formed, as revealed by broadband fluorescence in both the ultraviolet and visible regions. Note that all the broadband fluorescence results were obtained using either low-power continuouswave excitation (visible light) or unfocused excitation (pulsed, ultraviolet light), and thus laser-induced photolysis is not expected. Figure 7 presents these fluorescence profiles, which reveal three distinct contributions. In the ultraviolet region the small, "outside" peak occurs at the same location as the C_2 production profile and shows a fluorescence maximum at 310 nm. On the other hand, the larger "inside" peak moves sharply toward the burner centerline with increasing height and exhibits a fluorescence maximum at 345 nm. The peak of the visible fluorescence profile occurs between these two ultraviolet profiles and parallels the C₂ production profile with increasing height.

Figure 8 presents the ultraviolet fluorescence spectra obtained at two spatial locations in the methane/air diffusion flame. Previous work on premixed flames by Fujiwara et al. [48] revealed broadband fluorescence emission which peaked at 335-340 nm when excited at ~ 290 nm. The present profile measurements and the fluorescence spectra establish that two different molecules (or groups of molecules) exhibit ultraviolet fluorescence upon excitation at 282 nm. All of these broadband fluorescence features in the visible and ultraviolet regions have been attributed to polycyclic aromatic hydrocarbons (PAH) of approximately 2-4 rings [6-8, 12, 13, 15, 16, 48]. Numerous PAH species have been identified in hydrocarbon flames at concentration levels in the 1-50 parts per million range [49]. However, other molecules such as polyenes [50], polyynes [50], and 1-ring aromatic compounds [51, 52] may also contribute to the observed fluorescence spectra. These types of molecules are expected to exhibit broadband fluorescence in the ultraviolet and visible regions at elevated temperatures, and examples of each have been detected in our mass spectrometric profile measurements.

In the present measurements on the broadband laser-induced fluorescence, several pieces of evidence indicate that a low concentration of



Fig. 8. Laser-induced emission spectra observed at the two distinct spatial locations where broadband ultraviolet fluoresence occurs (see Fig. 7). Top spectrum: lateral position corresponding to the small, "outside" peak; height = 8 mm above the burner. Bottom spectrum: lateral position corresponding to the large, "inside" peak; height = 13 mm above the burner. The intensities of the spectra have been scaled for clarity. For these spectra only, 5% 1,3-trans-butadiene was added to the methane flow; this results in much stronger ultraviolet fluorescence signals while the profile location and shape remain the same as for the pure methane case.

molecules with strongly allowed optical transitions is responsible for the emission. For example, the visible fluorescence has been most difficult to detect using pulsed laser excitation. This result is consistent with a one-photon allowed optical transition which is easily saturated at high laser intensities. A small concentration of molecules with such optical properties is more readily detected using continuous-wave excitation, since each molecule can absorb and fluoresce many times during an observation period. In the ultraviolet region the detection of fluorescence using pulsed laser excitation is possible. This is due to a larger number of molecules which can absorb the ultraviolet radiation [53] and the fact that the cross section for excitation of fluorescence is larger in the ultraviolet region than for visible light [16]. However, the uv fluorescence signal is essentially saturated: reducing the laser intensity by a factor of five reduces the fluorescence signal by only 30% for unfocused beam conditions, and focusing the uv laser beam reduces the detected fluorescence signal sharply. Again, these results indicate that one-photon allowed electronic transitions are involved and are easily saturated.

C. Optical Measurements: Laser-Induced Ionization

In contrast to the one-photon laser-induced fluorescence measurements discussed above, the ionization of small soot particles requires high laser intensities and is a multiphoton process. Collisional quenching of the absorbed excitation energy is assumed to be slow relative to optical pumping rates, so that the profile measurements shown in Fig. 7 represent relative concentrations. This interpretation also assumes that the same size distribution of small particles is being ionized at various positions in the flame above the burner. The ionization signal grows by a factor of over 200 between 6 and 20 mm above the burner and occurs in the same location as the C_2 production profile and the small "outside," uv fluorescence profile.

The ionization of small soot particles (or very large molecules) using visible light is a key diagnostic measurement, since the resulting profiles locate the region in which the earliest soot particles are produced. At shorter wavelengths in the near ultraviolet region (280-310 nm, for example), laser-induced ionization also occurs readily using focused beams. However, the profiles show broadening toward the fuel zone, which is probably due to the ionization of small aromatic species. Both the optical and mass spectrometric results (see below) include profiles for aromatic molecules located to the fuel side of the soot ionization peaks. Aromatic species typically exhibit very strong absorption in the near ultraviolet region [53], which would facilitate two- and three-photon ionization. On the other hand, small aromatic molecules are expected to be much more difficult to ionize using visible excitation. Thus, the visible ionization profiles are thought to be particularly sensitive to very large molecules and small soot particles.

Table II summarizes information about the species profile measurements made using laser-induced fluorescence and ionization methods.

D. Mass Spectrometric Measurements

The concentrations of many stable species sampled with the quartz microprobe from the methane/air diffusion flame have been calibrated using mixtures of known composition—as described in the Experimental Section. Thus, the profile measurements for these molecules are reported in terms of absolute concentrations. Figures 9 and 10 present mole fraction profiles for the major species (CH₄, O₂, N₂, H₂, CO₂, and H₂O) at a height of 9 mm above the burner. Several points are noteworthy. First, the lateral position of stoichiometric burning, as indicated by the methane and oxygen concentrations approaching zero, is near the peak concentrations

Observation	Height above Burner Where Species Observed (mm)	Variation of Peak Intensity with Increasing Height
OH fluorescence	1–21	Decrease by 15%; profile broadens
C ₂ fluorescence	1-21	Increase by a factor of 125
Visible broadband fluorescence	9-21	Increase by a factor of 6
uv broadband fluorescence "outside peak"	3-9	Increase by a factor of 4
uv broadband fluorescence "inside peak"	5-21	Increase by a factor of 8
Soot ionization	6-20	Increase by a factor of 220

TABLE	П

Peak Intensity Variations Observed in the Optical Profile Measurements



Fig. 9. Mass spectrometric profile measurements of some of the major species: methane, nitrogen, oxygen, and water at a height of 9 mm above the burner. The N₂ profile has not been corrected for the small amount of CO detected at the same mass (see Fig. 10). At the top of the figure the sum of the mole fractions of all the species presented in Figs. 9 and 10 is shown; the dashed line represents the average value of 1.01 ± 0.04 .

of carbon dioxide and water and also coincides with the region of maximum temperature (Fig. 2). The peak in the OH concentration profile lies farther from the burner centerline (Fig. 6) and is thus slightly to the lean side of the position of stoichiometric burning. Secondly, a significant concentration of nitrogen is observed near the center of the flame, indicating that substantial convection and diffusion of air occur. The velocity measurements (Figs. 4 and 5) illustrate the convective transport of air toward the burner centerline. Finally, the calibration methods used here can be evaluated by summing the concentrations of the major species across the entire flame. The result is a nearly constant mole fraction total of 1.01 ± 0.04 .

Recently, several papers have presented analyses which show that the major species concentrations in a diffusion flame are a function only of the mixture fraction [54] or the local equivalence ratio, ϕ [13, 30]. Mitchell et al. [30] defined the local equivalence ratio as the number of oxygen atoms required for stoichiometric burning divided by the number of available oxygen atoms present. This quantity can be determined from measured species concentrations:

$$\phi = \frac{4[CH_4] + [H_2] + [CO] + [H_2O] + 2[CO_2]}{[H_2O] + [CO] + 2[CO_2] + 2[O_2]} . (12)$$

Of the required concentrations, all except that of



Fig. 10. Mass spectrometric profile measurements of hydrogen and carbon dioxide at a height of 9 mm above the burner. The calculated carbon monoxide profile and the local equivalence ratio ϕ are also shown (see text).

CO have been quantitatively measured (Figs. 9 and 10). In the present experiments CO and N_2 are monitored simultaneously at mass 28. However, if one assumes that the water-gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is equilibrated, then the concentration of CO can be determined from the measured concentrations of H_2O , CO_2 , and H_2 and the equilibrium constant for this reaction. Using [55]

 $K_{\rm p} = 0.039 \, \exp[6951 \, \operatorname{cal}/RT],$

a CO profile was determined and is shown in Fig. 10.

Below 1500K the water-gas shift reaction

may not be fully equilibrated [55], and thus the CO concentrations determined in the cooler regions of the flames are likely to be in error. Fortunately, the CO concentrations are small in these regions, and so the errors in calculating the local equivalence ratio are also small. Figure 10 presents the local equivalence ratio as a function of lateral position at a height of 9 mm in the methane/air diffusion flame.

Profile measurements for several intermediate hydrocarbons are shown in Fig. 11 for a height of 9 mm above the burner. The positions of peak intensity for acetylene, diacetylene, butadiene, and benzene are essentially identical and occur well to the fuel side of the high temperature zone. Additional profiles were obtained for triacetylene, vinylacetylene, methyl-



Fig. 11. Mass spectrometric profile measurements of several minor species: acetylene, benzene, diacetylene, and butadiene at a height of 9 mm above the burner. The peak concentrations in terms of mole fractions at this location are 6.2×10^{-3} for acetylene, 8.0 $\times 10^{-4}$ for benzene, 5.7 $\times 10^{-4}$ for diacetylene, and 1.1×10^{-4} for butadiene.

acetylene (and/or allene), and toluene, all of which exhibit peak concentrations at the same lateral position. This region rich in intermediate hydrocarbons occurs just to the fuel side of the location where C_2 production, the "outside," broadband uv fluorescence peak, and the soot ionization signals exhibit maximum intensity.

Figure 12 compares the evolution of the acetylene and benzene profiles as a function of height in the flame. A substantial concentration of acetylene is detected at the lowest height sampled (3 mm), and the profile extends well into the fuel region. For higher positions above the burner, the peak concentration first increases and then levels off. In contrast, the

benzene profiles exhibit quite different behavior. Low in the flame very little benzene is detected. However, at greater heights above the burner the peak concentration increases sharply, and the benzene concentration remains low at the burner centerline. Since the acetylene concentration is high early in the flame, acetylene must be formed rapidly during the pyrolysis of methane. This result has been widely observed in both flames [56] and pyrolysis studies [57]. Benzene, on the other hand, is formed later and is produced in a region rich in acetylene. The behavior of the other intermediate hydrocarbons detected in this work is similar to that of benzene. The only exceptions are diacetylene and triacetylene, which behave as acetylene, and



Fig. 12. Comparison of mass spectrometric profiles of acetylene and benzene at heights of 3, 9, and 15 mm above the burner. For each molecule one-half of the profile scans are presented.

butadiene, which exhibits profiles with small peak concentrations remaining constant with height above the burner.

IV. DISCUSSION

The species profile measurements can be summarized by plotting the peak intensities of the number densities as a function of height above the burner. Figure 13 presents the results for relative concentrations determined from the optical profiles and some of the absolute concentrations measured by mass spectrometry. All of the peak positions have been determined by simply measuring the distance between the two observed peak locations and then dividing by two. The profile for visible broadband fluorescence has been corrected for quenching effects, as discussed in Section III.B (the original data have been divided by the square root of the temperature). This analysis has the effect of moving the peak intensity location a little farther in toward the burner centerline. Thus, three optical signatures have been used to detect broadband fluorescence, which occurs in three spatially distinct locations. However, the broadband fluorescence profiles are sufficiently wide so that all three profiles do overlap each other to some extent.

Figure 13 reveals that the products of chemical growth reactions, including small soot particles, are found in a well-defined, spatially



Fig. 13. Location of maximum number density plotted for several species detected in the optical and mass spectrometric profile measurements. The left-hand side of the methane/ air diffusion flame is shown. Legend: OH, A; soot ions, \triangle ; ultraviolet PAH fluorescence ("oustide" peak), \bigcirc ; C₂ production, \diamond ; visible PAH fluorescence, \bigcirc ; acetylene, \blacksquare ; butadiene, \Box ; benzene, \times ; and ultraviolet PAH fluorescence ("inside" peak), \blacklozenge .

localized region well to the fuel side of the zone of maximum temperature (which closely parallels the OH profile). The earliest soot particles, as observed by laser-induced ionization, are formed at the high temperature edge of a region which is rich in intermediate hydrocarbons. In particular, the photolysis precursors of the C_2 radicals are abundant, as well as the molecules which exhibit broadband ultraviolet and visible fluorescence. These fluorescing species are assumed to be polycyclic aromatic hydrocarbons, but polyenes and polyynes may also contribute. It is interesting and puzzling that one of the uv broadband fluorescence peaks (the large, "inside" feature, Fig. 7) exhibits a profile which

maximizes far to the fuel side of any species detected in this work. These fluorescing molecules seem to be unconnected with chemical processes which lead to soot formation.

With increasing height above the burner the species profiles closely follow temperature isotherms, as opposed to velocity streamlines. This important result can be seen by comparing Fig. 13 with Figs. 3 and 5. In terms of the uncorrected thermocouple temperatures, the soot ionization profile is located in a 1500–1600K region, acetylene and other hydrocarbon combustion products are found at 1300K, and the unusual uv fluorescence profile follows a 1000K isotherm. If a radiation correction of 30–50K is added to the thermocouple temperatures (see Table I), then the products of condensation reactions (including intermediate hydrocarbons and small soot particles) exhibit maximum intensities in a region at 1300–1650K. In order to determine where the maximum production rates for these species occur, it will be necessary to analyze the concentration data in terms of the time-temperature history along streamlines, taking diffusion effects into account. One expects to find that the peak production rates will occur at different spatial locations and different temperatures than those which characterize the regions of maximum concentration.

At the higher positions of our measurements (15 mm and above) the Rayleigh scattering profiles show evidence for soot particles, with the peak location occurring slightly to the fuel side of the soot ionization signals. The scattering measurement is more sensitive to large particles than the ionization signals, and these larger particles are likely to be convected from the soot inception zone into the fuel region as they follow the flow streamlines [58].

The detailed steps which are involved in the early chemical growth reactions leading to soot inception are not yet established. Analysis of the species profile measurements indicates that a number of intermediate hydrocarbons may be important in the formation of the earliest soot particles. These profiles also provide some tantalizing clues regarding which specific molecules are most essential. Low in the methane/air diffusion flame, laser-induced C₂ production is observed. With increasing height above the burner the profile of C_2 production closely overlaps an ultraviolet fluorescence profile and the formation of the small particles detected by laser-induced ionization. The intensity of the C_2 production signals and the soot ionization signals both increase sharply with increasing height above the burner (see Table II). It is not known which molecule or molecules are photolyzed to yield C₂ [59]; with increasing height their concentration increases rapidly.

The present measurements which characterize the region of soot inception are entirely consistent with earlier experimental investigations of soot formation carried out using a Wolfhard-Parker burner [7, 10, 11]. Those studies involved scattering/extinction measurements on the soot field. Thus, the soot formation process was probed later in time than the optical and mass spectrometric results reported here. Kent and Wagner [11] found that the particle generation rate follows the flame contour, i.e., the temperature contours. Particle formation occurs in only one region having the appropriate fuel/ air ratio, temperature, and proximity to the radical-rich reaction zone [7]. These conclusions and our results are to be expected, since soot inception is a chemical process and chemical reaction rates are determined primarily by the temperature. Kent and Wagner [11] also found small particle diameters in the center of the fuel zone in their ethylene/air flame, although it was not possible to determine their number density. For our methane/air diffusion flame there is no evidence that soot formation occurs in the center of the fuel region up to a height of 21 mm.

In view of Kent and Wagner's comments on particle generation conditions [11], it is interesting to analyze the species profile data in terms of the local equivalence ratio, ϕ . This approach has been used successfully to correlate molecular species composition data over fairly broad regions of several diffusion flames [30, 54]. In particular, data for the major species taken at different flame positions can be collapsed onto a single curve for each species by plotting the measured concentrations versus ϕ . As described in the Results Section, our mass spectrometric measurements enable one to calculate the local equivalence ratio as a function of position in the methane/air diffusion flame (see Fig. 10). Using these results, our data at several heights above the burner for CH₄, O₂, H₂O, CO₂, and H₂ concentrations do fall on a single curve for each species. Figure 14 presents the data for CO_2 . In addition, the temperature data also collapse onto a single curve. However, this analysis is not successful for any of the species which have strongly varying peak concentrations as a function of height above the burner. Figure 14 shows the data for the benzene profile measurements



Fig. 14. Mole fraction results plotted against the local equivalence ratio: (top) carbon dioxide and (bottom) benzene data at heights of 4, 10, and 16 mm above the burner.

plotted in terms of the local equivalence ratio; the profiles at different heights are clearly distinguishable. These results show that in the soot inception zone in our methane/air diffusion flame the condensation reactions which produce intermediate hydrocarbons do not involve reversible, fully equilibrated chemical processes. Therefore, a more sophisticated analysis will be required in order to determine production and destruction rates for these species from the measured concentration profiles. This will involve following the time-temperature history for each species along velocity streamlines and accounting for diffusion effects.

V. CONCLUSIONS

- In a methane/air diffusion flame burning at atmospheric pressure, the products of condensation reactions are found in a localized region approximately 2-3 mm on the fuel side from the zone of maximum temperature. These intermediate hydrocarbons exhibit maximum concentrations at temperatures of ~1300-1650K. The earliest soot particles are detected at the high temperature edge of this region, which is rich in aromatic compounds and other unsaturated hydrocarbons.
- 2. The peak intensities in the species profiles closely follow temperature contours, indicating the dominant role of chemical reactions in the formation of intermediate hydrocarbons and the earliest soot particles.
- 3. Broadband fluorescence has been observed in the near ultraviolet and visible regions. For the ultraviolet emission, two spatially distinct contributions have been detected; their profiles exhibit different behavior as a function of height above the burner. All of the broadband fluorescence features have been attributed to polycyclic aromatic hydrocarbons, although many other species may also contribute at elevated temperatures.
- 4. An analysis of the species concentration profiles in terms of the local equivalence ratio successfully correlates the data for the major species (CH₄, O₂, H₂, CO₂, and H₂O), but is not adequate for any of the profile

results on the intermediate hydrocarbons or for the small soot particles.

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