Methyl Radical Concentrations and Production Rates in a Laminar Methane/Air Diffusion Flame

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Abstract—Methyl radicals have been detected in a laminar methane/air diffusion flame via an application of the scavenger probe technique. In these experiments, a quartz microprobe was modified such that iodine vapor was pumped from a storage side arm into the inside tip of the probe. Sampled methyl radicals react quantitatively with iodine to produce methyl iodide, which was detected by a mass spectrometer. The resulting quantitative profiles are compared to profiles of stable intermediate hydrocarbons which have been observed in this flame, as well as to profile signals which are due to methyl radical ionization by laser radiation. The concentrations of methyl are combined with velocity and temperature data to calculate the net rate of chemical reactions of methyl radical in the flame. The use of methyl radical concentration and rate data to estimate the concentrations of other reactive species is discussed.

INTRODUCTION

The goal of recent work in this laboratory has been to develop an understanding of the soot formation process in laminar diffusion flames (Smyth *et al.*, 1985; Miller *et al.*, 1986). Our approach has been to combine measurements of velocity, temperature, and species concentrations to extract information on the net rates of chemical processes. The resulting production rate data can then be used to evaluate specific reaction pathways leading to aromatic structures, which are thought to be the key building blocks in the soot formation process. Unfortunately, this effort has been hampered by a lack of species-specific, quantitative concentration profiles for highly reactive participants (such as free radicals and ions) in the growth chemistry.

The methyl radical is an important species in hydrocarbon flames in general and in methane flames in particular. It is involved in flame ignition and propagation reactions (via hydrogen abstraction from methane by H and OH). In methane flames, methyl radical recombination leads to the first two-carbon species and thus is the first important step in condensation pathways leading to soot (Warnatz, 1981). Further, methyl substitution on aromatic structures may result in an enhancement in reactivity of the incipient soot nuclei (Bittner and Howard, 1981). Methyl is thus a key actor in the soot formation process and profiles of its concentration are an important addition to the data set which has been accumulated for our flame system.

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In recently published work from this laboratory (Smyth and Taylor, 1985), relative profiles of methyl concentrations were observed using multiphoton ionization spectroscopy in a methane/air flame burning under identical conditions to those reported in our earlier studies (Smyth *et al.*, 1985). Methyl radicals occur just to the fuel rich side of the high temperature reaction zone adjacent to regions of the flame rich in intermediate hydrocarbons such as acetylene and benzene (Smyth *et al.*, 1985). The optical profiles of methyl were found to be spatially narrow low in the flame but appeared broadened with height above the burner due to interference in the measurement from ionization of small soot particles and larger hydrocarbons. Thus, the optical profiles presently provide only qualitative information about methyl concentrations over a limited region in this flame.

Radical scavenger microprobe sampling has been used as a method for the determination of radical concentrations in high temperature gaseous flow systems (Fristrom, 1963a, 1965, 1983). In this technique, a scavenger species is added during the sampling process and reacts with the unstable molecule under investigation to yield a stable product which can be detected later in the sampling train. The radical concentration is then deduced from the scavenging reaction equilibrium. The success of the technique requires that the scavenging reaction proceeds at a rate faster than reactions within the probe (including wall reactions) which might alter the concentrations of the species under investigation. The technique has successfully been applied to the determination of methyl concentrations in a premixed methane–oxygen flame with molecular iodine used as the scavenger (Fristrom, 1963b).

In this paper the implementation of radical scavenging for the detection of methyl radical in a laminar, methane/air diffusion flame is demonstrated. Profiles of the methyl radical concentration at various flame heights are combined with velocity and temperature data to calculate the net chemical production rate for methyl. The use of the concentration and rate data to estimate other radical and atom concentrations in the flame is discussed.

EXPERIMENTAL PROCEDURE

The burner and mass-spectrometric sampling systems have been described in detail previously (Smyth *et al.*, 1985). Modifications to this apparatus and experimental procedure will be summarized below. A laminar methane/air diffusion flame burning at one atmosphere pressure was supported on a Wolfhard/ Parker slot burner. The burner body consisted of an 8×41 mm fuel slot located between two 16 mm wide air slots (see Figure 1). Two flame sheets are created at the air–fuel interfaces and lateral profiles of concentration are symmetric about the plane running through the center of the burner. A rectangular, wire screen chimney with "gulls" similar to that described by Kent *et al.* (1981) was used to stabilize the flame.

In our previous work (Smyth *et al.*, 1985), a quartz microprobe was inserted into the flame parallel to the fuel/air slot separators. The microprobe, which was based on the design criteria of Fristrom and Westenberg (1965), had an orifice diameter of approximately 140 μm with an effective probe volume diameter of 700 μm. The sampled gas enters a region (≈ 0.3 torr) pumped by a rotary vacuum pump. A second microprobe sampled gas from this region into the ionizer of a quadrupole mass spectrometer. The burner was mounted on a programmable micrometer stage whose position was controlled by a computer. Concentration
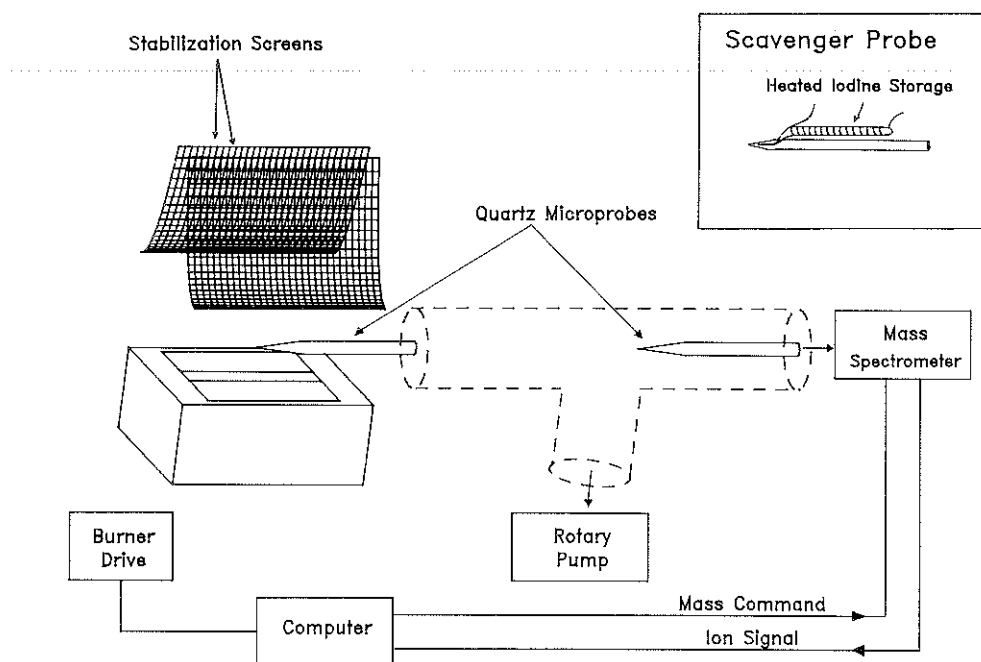
FIGURE 1 Diagram of the slot burner and sampling system used in methyl radical profile studies. Both probes had orifice diameters of ≈ 140 m. The pressure in the region between the probes was typically 0.3–1 torr.

profiles were obtained by moving the burner laterally under the fixed microprobe while monitoring a specific mass ion signal from the mass spectrometer. The mass spectrometer was typically operated at an electron ionization energy of 20 eV to minimize fragmentation processes. The gradients of concentration are much steeper in the lateral versus the vertical dimensions in this flame. Thus, profile data points were collected every 0.2 mm in the lateral direction and consecutive profiles were obtained every 2 mm in height.

In the present experiments, the first microprobe was modified by attaching a small vial containing molecular iodine to the side of the probe (see inset, Figure 1). A 1 mm o.d. quartz tube ran from the iodine vial, through the side wall of the probe, and to the front of the sampling probe. The distance from the orifice in the tip of the probe to the end of the iodine supply tube was ≈ 1 mm. The iodine storage area could be heated to vary the vapor pressure of iodine in the sampling vial and, hence, its concentration within the probe.

A calibration scheme was presented previously for the conversion of raw profile signals from the mass spectrometer into absolute concentrations (Smyth *et al.*, 1985). In this analysis it was shown that the observed signal intensity is proportional to the molecular flow rate through the orifice in the first sampling probe. The proportionality factor could be determined by measuring a calibration factor for a species in a mixture with argon at room temperature and then correcting this calibration factor for the variation of flow rate with temperature. [Profiles of temperature in this flame are described in a prior publication (Smyth *et*

al., 1985).] For species which could not be calibrated directly, calibration factors for species with similar masses, ionization potentials, and molecular structure were used after correcting for the relative efficiencies of electron ionization. For example, the calibration factor for toluene was applied to the benzene profile measurements.

Application of this calibration scheme to methyl radical determinations is complicated by the fact that the species which enters the sampling probe (methyl) is different than the molecule which traverses the second probe and is eventually ionized (methyl iodide). Our calibration data for a wide range of sampled species indicate that the critical factor in the overall sampling process is the temperature dependence of the molecular flow through the first orifice. We have chosen to apply the calibration factor for methane, which is similar in molecular structure and mass to methyl radical, to the quantification of methyl iodide profiles after correcting for the relative ionization efficiencies of the two molecules. The ionization cross-sections at 70 eV for methane and methyl iodide were estimated by a semi-empirical method proposed by Beran and Kevan (1969) (CH_4, 4.67×10^{-16} cm^2; CH_3I, 11.27×10^{-16} cm^2). The ratio of the ionization cross-sections at 20 eV is taken to be the same as that at 70 eV (Smyth *et al.*, 1985).

The reaction of methyl radical with iodine is particularly favorable to study via this probe technique. Not only is there likely to be a high concentration of methyl in this flame (relative to other hydrocarbon radicals), but the reaction to form methyl iodide is fast (Fristrom, 1963b), and the equilibrium greatly favors the formation of methyl iodide ($K_{eq} > 10^{20}$ for probe temperatures between 800 and 1500 K). Further, iodine atoms form only weak bonds with carbon and are unlikely to initiate additional hydrocarbon chemistry in the probe. Both the completeness of the reaction and the lack of complicating chemistry were confirmed by heating the iodine storage arm such that the calculated molecular iodine vapor pressure varied from 2 to more than 100 torr. No change in the observed CH_3I signal intensity or profile shape were observed.

METHYL RADICAL CONCENTRATIONS

Profiles of methyl radical concentration expressed as mole fraction are reported in Figure 2 for three flame heights. The profiles are more spatially narrow than profiles which have been reported for other intermediate hydrocarbons (Smyth *et al.*, 1985). Further, unlike the majority of hydrocarbon species observed in this flame, the concentration of methyl does not systematically vary as a function of height in the flame.

Because there may be some loss of methyl due to recombination within the probe, these reported concentrations might be expected to represent lower limits of the actual methyl radical mole fractions. However, although the recombination rate of methyl radicals [$k = 1.68 \times 10^{-9}\ T^{-0.64}$ cm^3/(molecule·sec), Tsang and Hampson, 1985] is faster than the reaction of methyl radicals with iodine [$k = 3.3 \times 10^{-12}$ cm^3/(molecule·sec), Fristrom, 1983], the concentration of iodine is 5000 times greater than that of methyl radicals and recombination should not be an important interference in the present measurements.

Prado *et al.* (1984) have reported a shift in profile peak locations for polynuclear aromatic hydrocarbons sampled with a quartz microprobe relative to profiles of a laser-induced fluorescence signal which have been attributed to the same class of molecules. Disturbances of the measured flame structure such as
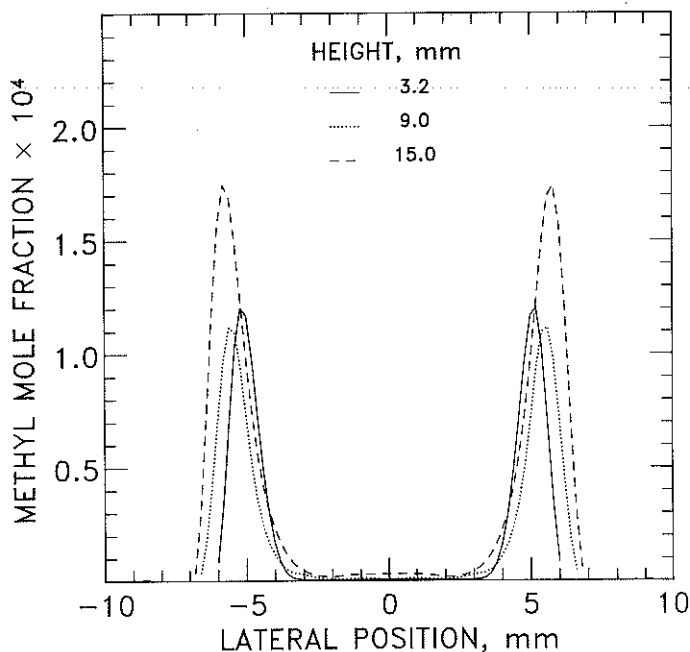
FIGURE 2   Methyl radical concentrations at three heights in the flame.

these seriously hamper our ability to unravel diffusion flame chemistry. Consequently, agreement between profiles collected with optical versus mass spectrometric techniques is an important test of our approach.

Figure 3 compares the methyl radical profile as observed with the scavenger probe technique with that previously reported for multiphoton ionization (Smyth and Taylor, 1985). The methyl radical concentrations for the mass spectral measurements are the absolute number densities; it is assumed that the optical ionization signal is proportional to the number of methyl radicals within the laser probe volume. Figure 3 shows that the mass spectrometric probe profile is slightly broadened relative to the optical profile. This is to be expected because of the greater spatial resolution of the optical technique (the laser beam waist is estimated to be $\leqslant 100$ μm) relative to the quartz microprobe. However, there does not appear to be a significant difference in the location of the maximum or the shape of the profile peak.

Figure 4 follows the position of maximum methyl number density with height in the flame. Also shown are the analogous traces for a number of other intermediate hydrocarbons from our previous mass spectral sampling studies, OH radical concentrations from fluorescence measurements, and soot particle number densities from laser-ionization measurements (Smyth et al., 1985). These data indicate that methyl appears in a region of the flame between the high temperature reaction zone and cooler, richer regions where soot particles and intermediate hydrocarbons are observed. It should be noted that these traces follow the peaks in concentrations; the profiles overlap to some extent due to the spatial distribution of the species within the flame.
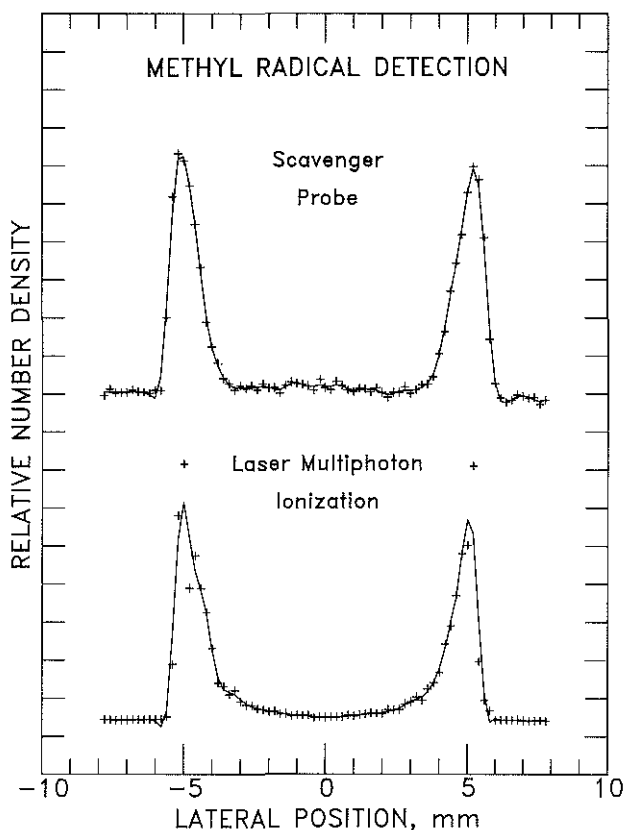
FIGURE 3   Comparison of methyl radical profiles obtained from mass spectrometric (top) and laser multiphoton ionization probes (bottom, from Smyth and Taylor, 1985) at a height of 3 mm above the burner. The optical technique produces profiles of relative methyl number density; absolute number densities are plotted for the mass spectrometric profile.

PRODUCTION RATE ANALYSIS FOR METHYL

In a laminar flame, the molecular fluxes into and out of a particular region are equal to one another and the observed concentration does not change as a function of time. This implies that the change in concentration due to transport processes balances that due to chemical reactions:

$$R_i = \nabla[N_i(v + V_i)] . \tag{1}$$

Here, R_i is the net chemical production rate, N_i is the molecular number density, v is the convective velocity, and V_i is the diffusion velocity. The solution of this species conservation equation has been used in the past to calculate the rate of chemical production of species in one-dimensional premixed flames (Cole *et al.*, 1984) and, more recently, in a laminar diffusion flame (Miller, 1985; Miller *et al.*, 1986).
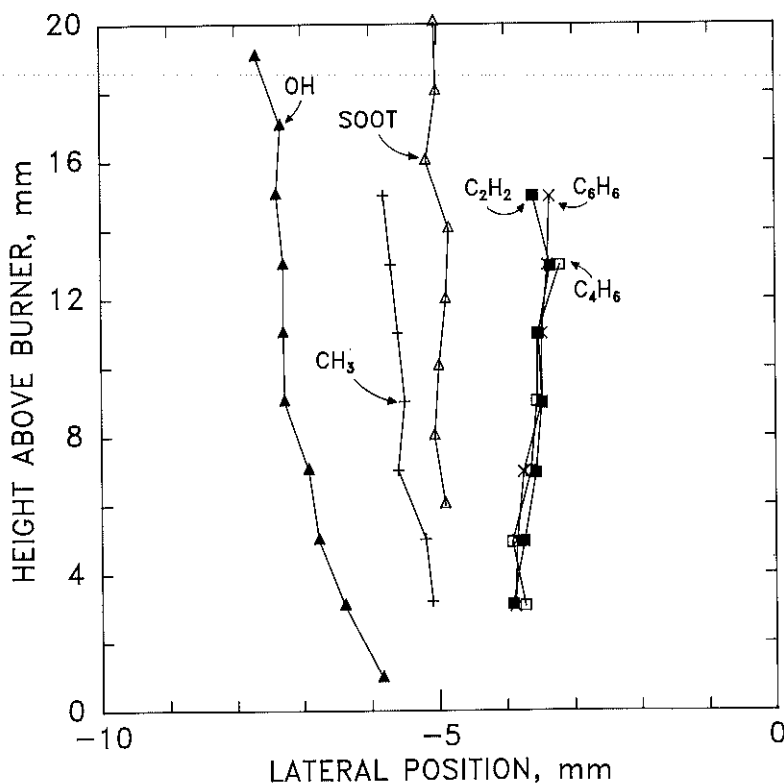
FIGURE 4 Location of maximum number density plotted as a function of flame position for methyl radicals as well as several species which were studied in previous work (Smyth *et al.*, 1985): OH radicals, ▲ (from laser induced fluorescence); incipient soot particles, △ (from laser ionization); acetylene, ■; benzene, ×; butadiene, □; and methyl, + (from mass spectrometric probe studies).

In earlier work (Smyth *et al.*, 1985) we reported profiles of the two components of convective velocity, v, as determined by laser Doppler velocimetry. The diffusion velocity is given by (Fristrom and Westenberg, 1965):

$$V_i = - D_{i, \text{mix}} \left[\nabla \ln(x_i) + (k_T/x_i) \nabla \ln(T) \right], \tag{2}$$

where x_i is the mole fraction of species i, $D_{i, \text{mix}}$ is the diffusion coefficient for species i into the local mixture, and k_T is the thermal diffusion ratio. The mixture diffusion coefficient is calculated from the binary diffusion coefficients for the interaction of species i with all major components in its local environment. The binary diffusion coefficients are calculated using the method outlined by Fristrom and Westenberg (1965).

Thermal diffusion is often ignored in the solution of the species conservation equation for premixed flame systems. In diffusion flames, the temperature gradients are quite steep (2000–3000 K/cm) and it is less clear whether thermal diffusion can be legitimately disregarded. Unfortunately, calculation of thermal diffusion ratios for mixtures is complex (Hirschfelder *et al.*, 1954). In an effort to evaluate the importance of thermal diffusion for the present calculations we have used the

thermal diffusion ratio for methyl as the minor component in a binary mixture with nitrogen. This assumption is validated by the observations that nitrogen is the dominant flame species (nitrogen mole fraction > 0.5) in regions where methyl is observed and that the binary thermal diffusion ratios of methyl with other prevalent flame species are smaller in absolute magnitude than that with nitrogen.

The rate of chemical production or destruction is calculated by numerically differentiating Eq. (1) using profiles at a particular height as well as profiles obtained for heights above and below. Because a great number of profiles are required for each production rate calculation, initial smoothing and centering of the input data sets was required. The data smoothing algorithm was based on the technique proposed by Savitsky and Golay (1964).

Figure 5 presents profiles of molar fluxes which contribute to the observed concentration profile at a height of 5 mm above the burner. It is interesting to note that the magnitude of the thermal diffusion contribution is quite small at all lateral positions relative to those arising from concentration-driven diffusion and convection. This observation supports the simplification of the thermal diffusion calculation as discussed above.

DISCUSSION AND CONCLUSIONS

Methyl is produced in a region of the flame where oxygen and methane concentrations approach zero and the temperature reaches its highest observed value (> 1900 K). As methyl diffuses or is convected away from this production area, destruction processes in both lean and rich regions of the flame eliminate it. The prominent features of the methyl production rate profile are qualitatively simple to understand. Methyl radicals are formed near the high temperature reaction zone of the diffusion flame by hydrogen-atom abstraction from methane by H and OH. As the radicals move into the cooler, richer regions of the flame, loss processes such as recombination to form ethane and reaction with molecular hydrogen dominate the net rate profile. As methyl radicals diffuse outwards into the leaner regions, oxidative destruction processes overwhelm the formation pathways. Because methyl is destroyed effectively and with nearly equal net rates in both of these regions, the resulting concentration profile is both narrow and nearly symmetrical. This result is quite different from the production rate calculations for other intermediate hydrocarbons for which the only major destruction feature was on the lean edge of the concentration profile. For these species, such as benzene and acetylene, concentration profiles were broadened into cooler, richer regions of the flame.

Methyl radical concentration and production rate data provide only the first glimpse at the reactive pool of hydrocarbon radicals which are responsible for the structure of diffusion flames. Unfortunately, there are a number of limitations to this experiment which may prevent the application of iodine scavenging to the detection of other hydrocarbon radicals which are present in this flame. For example, the vinyl radical, which is thought to be critically important in soot particle inception processes (Frenklach et al., 1984; Colket, 1985; Cole et al., 1984), is more reactive than methyl, and thus more likely to be lost to wall reactions within the probe prior to the scavenging reaction. Further, in a premixed flame in which the acetylene concentration was 1%, the vinyl concentration was found to be only 3×10^{-5} (Bittner and Howard, 1981). This value is quite close to
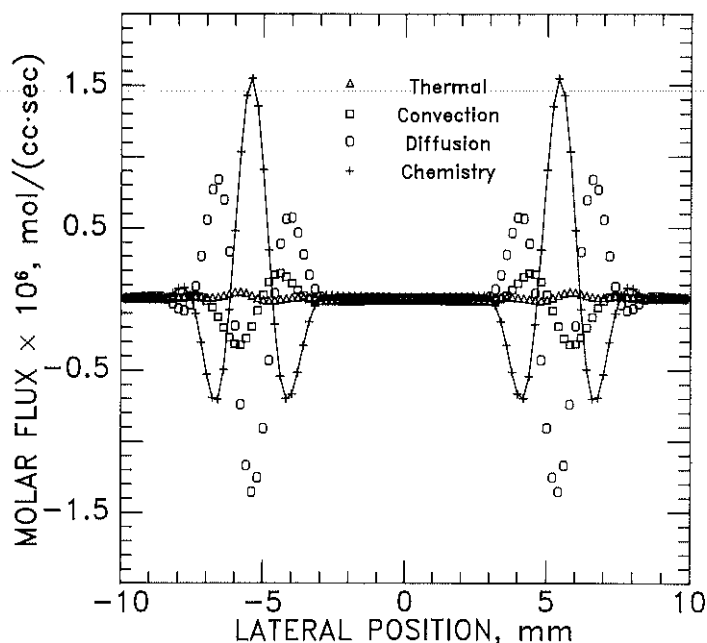
FIGURE 5 Molar flux terms which contribute to the observed methyl radical concentration at a height of 5 mm above the burner [see Eq. (1)]: △ –thermal diffusion, ○–regular diffusion, □–convection, + –net chemical rate.

our detection limit of 1×10^{-5} for methyl iodide. These two factors taken together would make iodine scavenging of vinyl difficult to observe.

It is possible, however, to use methyl concentrations to estimate concentrations for some of the other interesting radicals in this flame system. For example, the ethynyl radical, C_2H, reacts with methane to form acetylene and methyl radicals (Okabe, 1981). If it is assumed that this reaction is equilibrated, the concentration of ethynyl can be calculated from the other three concentrations and the equilibrium constant. A similar approach has been used to estimate the concentration of atomic hydrogen in the flame (Miller et al., 1986). It may also be possible to extract concentrations from the production rate data. For example, the lean (outer) destruction feature in the chemical rate profile of methyl may be dominated by the relatively irreversible reaction of methyl and oxygen atoms to form formaldehyde (Warnatz, 1981). From the magnitude of this feature and the observed methyl concentration, the O atom concentration would be estimated to be approximately 8 parts per million at this flame location (5 mm above the burner).

Methyl radical concentrations and their derived chemical production rates are a valuable addition to the data available to characterize the structure of hydrocarbon diffusion flames. Methyl concentration data are presently being used to estimate concentrations of reactive species in hydrocarbon condensation chemistry. These derived concentrations can then be used to critically evaluate proposed models for aromatic molecule and soot particle formation during hydrocarbon combustion. As this work illustrates, quartz microprobes are still a most valuable analysis tool for

atmospheric diffusion flames, and the scavenger probe modification extends the range of this approach to include the important problem of quantitative radical detection.

REFERENCES

Beran, J. A., and Kevan, L. (1969). Molecular electron ionization cross sections at 70 eV. *J. Phys. Chem.* **73**, 3866.

Bittner, J. D., and Howard, J. B. (1981). Composition profiles and reaction mechanisms in a near-sooting benzene/oxygen/argon flame. *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1105.

Cole, J. A., Bittner, J. D., Longwell, J. P., and Howard, J. B. (1984). Formation mechanisms of aromatic compounds in aliphatic flames. *Combust. Flame* **56**, 51.

Colket, M. M., III (1985). Pyrolysis of vinylacetylene. *Chemical and Physcial Processes in Combustion*, 53–1.

Frenklach, M., Clary, D. W., Gardiner, W. G., Jr., and Stein, S. E. (1984). Detailed kinetic modelling of soot formation in shock-tube pyrolysis of acetylene. *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 887.

Fristrom, R. M. (1963a). Scavenger probe sampling: A method for studying gaseous free radicals. *Science* **140**, 297.

Fristrom, R. M. (1963b). Radical concentrations and reactions in a methane–oxygen flame. *Ninth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 560.

Fristrom, R. M., and Westenberg, A. A. (1965). *Flame Structure*, McGraw-Hill, New York.

Fristrom, R. M. (1983). Comments on quenching mechanisms in the microprobe sampling of flames. *Combust. Flame* **50**, 239.

Gelles, E., and Pitzer, K. S. (1953). Thermodynamic functions of the halogenated methanes. *J. Am. Chem. Soc.* **75**, 5259.

Golden, D. M., Walsh, R., and Benson, S. W. (1965). The thermochemistry of the gas phase equilibrium $I_2 + CH_4 \rightarrow CH_3I + HI$. *J. Am. Chem. Soc.* **87**, 4053.

Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B. (1954). *Molecular Theory of Gases and Liquids*, John Wiley and Sons, Inc., New York, p. 1126.

Kent, J. H., Jander, H., and Wagner, H. Gg. (1981). Soot formation in a laminar diffusion flame. *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1117.

Miller, J. H. (1985). Chemical production rates of intermediate hydrocarbons in diffusion flames: Preliminary results for acetylene. *Chemical and Physical Processes in Combustion*, 11–1, November, 1985.

Miller, J. H., Mallard, W. G., and Smyth, K. C. (1986). Chemical production rates of intermediate hydrocarbons in a methane/air diffusion flame. *Twenty-first Symposium (International) on Combustion*, in press.

Okabe, H. (1981). Photochemistry of acetylene at 1470 Å. *J. Chem. Phys.* **75**, 2772.

Prado, G., Garo, A., Ko, A., and Sarofim, A. (1984). Polycyclic aromatic hydrocarbons: Formation and destruction in a laminar diffusion flame. *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1984, p. 989.

Savitsky, A., and Golay, M. J. E. (1964). Smoothing and differentiation of data by simplified least squares procedures. *Anal. Chem.* **36**, 1627.

Smyth, K. C., Miller, J. H., Dorfman, R. C., Mallard, W. G., and Santoro, R. J. (1985). Soot inception in a methane/air diffusion flame as characterized by detailed species profiles. *Combust. Flame* **62**, 157.

Smyth, K. C., and Taylor, P. H. (1985). Detection of the methyl radical in a methane/air diffusion flame by multiphoton ionization spectroscopy. *Chem. Phys. Lett.* **122**, 518.

Stull, D. R., and Prophet, H. (Eds.) (1971). *JANAF Thermochemical Tables*, 2nd Edition, *NSRDS-NBS*
    37.
Tsang, W., and Hampson, R. F. (1985). Chemical kinetic base for methane combustion. *NBSIR*
    84–2913.
Warnatz, J. (1981). The structure of laminar alkane, alkene, and acetylene flames. *Eighteenth
    Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 369.