## CHEMICAL PRODUCTION RATES OF INTERMEDIATE HYDROCARBONS IN A METHANE/AIR DIFFUSION FLAME

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The net production and destruction rates for acetylene, diacetylene, butadiene, and benzene have been determined from measurements of species concentration, temperature, and velocity in a methane/air diffusion flame. In addition, profile measurements of the methyl radical are used to compute profiles of hydrogen atoms. These results provide an initial evaluation of proposed models of hydrocarbon chemical growth routes in diffusion flames, and indicate that the vinyl radical plays a key role in the formation of benzene. Evidence is also presented for acetylene participation in surface growth processes on small soot particles.

## I. Introduction

The identification of the formation mechanism of large hydrocarbons produced during combustion is one of the most challenging problems in high temperature chemistry. Despite the complexity of chemical growth reactions in flames, there have been significant recent gains in our understanding. Extensive profile measurements have led to a detailed description of the chemical structure of premixed flames<sup>1-13</sup>. These results have been combined with the time-temperature history in one-dimensional flame systems to produce simple models for molecular growth. Modelling efforts have also been undertaken using shock tube data<sup>14-16</sup>.

Most practical combustion systems are diffusion flames. Here, in contrast to shock tubes and premixed flames, our knowledge of the soot formation process is much less complete. This is due in part to the lack of data which are required for a detailed modelling of diffusion flames and in part to the inherently more complex interactions between transport and chemical processes in these systems.

Recently, concentration measurements have been reported for molecular species, including intermediate hydrocarbons, in laminar methane/air diffusion flames<sup>17,18</sup>. Our work has shown that a knowledge of the local chemical composition is *not* sufficient to predict the concentrations of intermediate hydrocarbons, such as acetylene and benzene, and soot particles<sup>17</sup>. Therefore, in this paper an analysis is undertaken combining detailed species profile measurements, temperature, and convective velocity measurements to calculate production and destruction rates for intermediate hydrocarbons. The experimental values for the net production/destruction rates are compared with estimated rates of chemical growth reactions in order to evaluate possible formation routes of aromatic hydrocarbon species.

### **II. Experimental results**

Detailed species profiles have been measured in an atmospheric pressure methane/air diffusion flame using both mass spectrometric and optical techniques<sup>17</sup>. A Wolfhard-Parker burner was utilized, consisting of a central fuel slot and two adjacent slots for air. Two flame sheets were formed at the fuel/air interfaces, and all species profiles were symmetric about the burner centerline. Profiles of stable flame species were collected with a direct-sampling mass spectrometer equipped with a quartz microprobe (orifice diameter  $\approx 140 \ \mu m$ ). Calibration of the major species (methane, oxygen, nitrogen, carbon dioxide, carbon monoxide, water, and hydrogen) led to a mass balance across the flame (total mole fraction =  $1.01 \pm 0.04$ ). In addition, absolute concentrations of acetylene, butadiene, and toluene were determined using a direct calibration procedure. Profiles of methylacetylene (and/or allene), vinylacetylene, diacetylene, triacetylene, benzene, and naphthalene were also measured and calibrated indirectly<sup>17</sup>.

In a related series of measurements<sup>19</sup>, a quartz microprobe was modified so that iodine vapor could be introduced into the inside of the quartz tube. Sampled methyl radicals react quantitatively in the tip of the scavenger probe to form methyl iodide<sup>20-22</sup>, which can then be detected in the mass spectrometer.

The optical measurements included laserinduced fluorescence, multiphoton ionization, photodissociation, and Rayleigh scattering investigations of the methane/air diffusion flame<sup>17,23</sup>. These studies have produced profiles of relative OH and methyl radical concentrations, as well as larger hydrocarbon species and small soot particles.

Temperature profiles were measured with an uncoated 125 µm diameter fine wire Pt/Pt-10% Rh thermocouple. Corrections due to radiation effects were estimated to be less than 7% at the highest temperatures in this flame<sup>17</sup>, while catalytic effects are expected to be small<sup>24</sup> and in the opposite direction. For equilibrium and kinetic calculations discussed in Section IV, the original temperature data were corrected for the estimated radiation effect. Both the horizontal and vertical components of the convective velocity were determined using laser Doppler velocimetry. The gradients in concentration and temperature in this flame are steepest in the lateral direction. Therefore, profile data points were collected every 0.2 mm horizontally and every 2 mm in the vertical direction.

Figure 1 illustrates the temperature and velocity fields for this flame. Shown as solid lines are isothermal contours determined from the thermocouple profiles. Also shown are streamlines of convective velocity calculated from the two measured velocity components. The streamlines exhibit trajectories which originate in the lean region of the flame, cross the high temperature, primary reaction zones, and continue into the fuel-rich regions.

Figure 2 presents profiles collected for several intermediate hydrocarbons: acetylene, benzene, diacetylene, and butadiene. Peak concentrations for these species are 6200, 800, 570, and 110 parts per million, respectively, at this height. Profiles obtained for the other intermediate hydrocarbons all exhibit concentration maxima in the same region of the flame.



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



FIG. 2. Mass spectrometric profile measurements of several minor species: acetylene, benzene, diacetylene, and butadiene at a height of 9 mm above the burner.

### **III. Production Rate Calculation**

### A. Procedure

A primary goal of this work is to apply kinetic modelling to a methane/air diffusion flame; that is, to compare the predictions of models which have been used to describe premixed flame and shock tube results with our diffusion flame data (see Section IV, below). A viable model must not only account for the steady state concentrations in species involved in chemical growth processes, but also for the chemical flux of these species in the flame. To make this comparison, the net chemical production and destruction rates for individual species have been computed from concentration, temperature, and velocity measurements, as described below.

A laminar flame is a steady-state system, and thus the value of any macroscopic variable does not change with time at a particular spatial location. Therefore, the net flux for each species into a given volume element due to convective and diffusive transport must be balanced by a corresponding change in the species concentration due to chemical reactions:

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

Here ,  $R_i$  is the net chemical rate,  $N_i$  is the species concentration, v is the convective velocity, and  $V_i$  is the net diffusion velocity of the species into the local mixture. The rate of chemical production is computed by numerical differentiation of Eq. 1 using profile data at a particular height, H, as well as data from  $H \pm 2$  mm. Due to extreme sensitivity to noise in this calculation, it is important that the data be smooth. Thus, all of the input data sets were passed several times through a Savitsky-Golay digital filter<sup>25</sup> before differentiation.

The diffusion velocity is given by<sup>26</sup>:

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

where  $x_i$  is the mole fraction of species i,  $D_{i,mix}$  is the diffusion coefficient for species i into the local mixture, and  $k_T$  is the thermal diffusion ratio. In this work,  $D_{i,mix}$  was determined from the contributions of all molecules present in the flame at concentrations greater than 1% (nitrogen, oxygen, water, carbon dioxide, carbon monoxide, hydrogen, and methane) and is given by:

$$D_{i,\min} = (1 - x_i) \left/ \left[ \sum_{\substack{j=1\\ j \neq i}} (x_j / D_{ij}) \right] \right.$$
(3)

where  $D_{ij}$  are binary diffusion coefficients calculated using the method of Fristrom and Westenberg<sup>26</sup>.

The calculation of the thermal diffusion ratio is difficult for binary mixtures and is much more complicated in multi-component systems<sup>27</sup>. If the temperature gradients are small enough, the first term in Eq.2 (concentration-driven diffusion) dominates the second (thermal diffusion), and the contributions of thermal diffusion to mass transport can be ignored. The horizontal temperature gradients in our flame are steep in certain locations (2000-3000 K/cm), and thus thermal diffusion cannot be dismissed. To critically evaluate the importance of thermal diffusion,  $k_T$  has been calculated as a function of temperature and composition for a variety of binary mixtures. Our results indicate that the ratio  $k_T/x_i$  is insensitive to the concentration of the minor component. Further, at high temperatures (>1000 K),  $k_T/x_i$  is relatively independent of temperature. Therefore, it is possible to select a value of  $k_T/x_i$  which represents a "worst case" for the thermal diffusion contribution to the calculated production rate for a given species in order to test the hypothesis that thermal diffusion is not significant. (See next section)

### **B.** Production Rate Calculation Results

Figure 3 presents the diffusive (concentration-driven and thermal) and convective contributions to the calculated production/destruction rate for acetylene at a height of 9 mm above the burner. Convection transports material across the high temperature reaction zone towards the burner centerline (see Fig. 1). In contrast, diffu-



FIG. 3. Contributions to the net flux of acetylene at 9 mm above the burner:  $\triangle$ : thermal diffusion,  $\bigcirc$ : concentration-driven diffusion,  $\square$ : convection, and +: chemical production and destruction. The actual molar flux due to the mass transport terms into a spatial region is opposite in sign to that shown in the figure.

sion away from the burner centerline brings acetylene into the high temperature oxidation region of the flame where it is destroyed.

For these calculations, a value of 0.18 was used for the magnitude of the ratio  $k_T/x_i$  for acetylene in methane. This estimate for the thermal diffusion contribution was the maximum calculated for acetylene interacting with major species (nitrogen, water, carbon dioxide, and methane) in regions of production and destruction rate peaks. The sign of the contribution from nitrogen and carbon dioxide interactions is opposite to that from methane and water. Thus, the overall thermal diffusion concentration would be smaller than that calculated above. As Fig. 3 illustrates, even under these worst case assumptions, the flux due to thermal diffusion is small with respect to convection and concentration-driven diffusion terms.

Figure 4 shows the evolution of the acetylene production rate with height above the burner and reveals that the chemical role of acetylene changes. Low in the flame the destruction rate exhibits a maximum value ( $R_i = -1.9 \times 10^{-5}$  mol/(cm<sup>3</sup> s)) near the high temperature, primary reaction zone, and the production rate feature ( $R_i = 3.1 \times 10^{-5}$  mol/(cm<sup>3</sup> s)) 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. 2). Higher in this flame it appears that the production rate peak



FIG. 4. Profiles of the net chemical production rate for acetylene at two heights in the flame (solid lines); only the left hand side of the flame is shown. Also shown is a profile of the small soot particle concentration<sup>17</sup> at a height of 12 mm above the burner (dashed line).

is diminished by a new destructive feature (see arrow in Figure 4). This feature showed a systematic evolution with height above the burner: it was absent in profiles below H = 10mm, it appeared as an inflection on the production rate feature at H = 11 mm, and as a dip in the 13 mm calculation. The new destruction feature is not an artifact of the data analysis since its location and appearance are unaffected by data smoothing.

Harris and Weiner have found that acetylene is the primary species responsible for soot particle growth in rich, premixed flames<sup>28-30</sup>. At short times the surface area available for growth of incipient soot particles was measured to be ~1.0 cm<sup>2</sup>/cm<sup>3</sup>, and a specific surface growth rate of ~8 × 10<sup>-5</sup> g/(cm<sup>2</sup> · s) was determined in ethylene flames<sup>28,29</sup>. Similar values have been reported for ethylene and propane diffusion flames<sup>31-34</sup>. In our experiments the location of the decrease in the acetylene production rate profile coincides with the peak concentrations of small soot particles detected in earlier profile measurements (shown as a dotted line on the right hand side of Fig. 4)<sup>17</sup>. If one assumes that these incipient soot particles in our methane/air diffusion flame exhibit surface areas and specific surface growth rates similar to those found in rich premixed flames and diffusion flames of other fuels, then the magnitude of the change in total soot mass can be estimated to be  $8 \times 10^{-5}$  g/(cm<sup>3</sup> s) or  $3 \times 10^{-6}$  acetylene mol/(cm<sup>3</sup> s). This value is consistent with the magnitude of the destruction feature shown in Fig. 4, and thus is attributed to surface growth chemistry on small soot particles.

The production rates for diacetylene, butadiene, and benzene have also been calculated. Figure 5 shows the net chemical rates for butadiene and benzene. Qualitatively, these profiles are very similar to those for acetylene: there is a destruction peak located near the high temperature reaction zone and a production rate feature located between the high temperature reaction zone and the observed peak in concentration of the species. Due to the diminished diffusion velocities of these heavier hydrocarbons relative to that for acetylene, the loss of these species by diffusion into the high temperature reaction zone is relatively less important, i.e., their time history more closely follows the streamlines calculated from the convective velocities.

### **IV. Molecular Growth Chemistry**

The chemistry of methane combustion to form carbon dioxide and water is reasonably



FIG. 5. Production rate profiles for benzene and butadiene at 9 mm above the burner.

well established<sup>35</sup>. However, the molecular growth steps which lead to the formation of polynuclear aromatic hydrocarbons (PAH) and soot particles are much less certain. Tanzawa and Gardiner<sup>14</sup> examined the mechanism of acetylene pyrolysis at temperatures ranging from 625 to 2500 K. They found that at low temperatures vinyl acetylene was a major product while at higher temperatures diacetylene was favored. Their analysis indicates that vinyl radical (C2H3·) was more important at temperatures less than 1250 K, whereas at higher temperatures the ethynyl radical, C<sub>2</sub>H·, chemistry is dominant. Colket studied the pyrolysis of acetylene and vinylacetylene in shock tubes from 1100 to 2400 K<sup>16</sup>. At temperatures below 1500 K his results indicate that the vinyl radical is the key species in the formation of benzene via:

R1) 
$$H \cdot + C_2H_2 + M = C_2H_3 \cdot + M$$
  
R2)  $C_2H_3 \cdot + C_2H_2 = C_4H_5 \cdot$   
R3)  $C_4H_4 \cdot = C_4H_4 + H_5 \cdot$ 

R4)  $C_4H_4 + C_2H_3 = C_6H_7$ 

$$\mathbf{R5}) \qquad \mathbf{C_6H_7} = \mathbf{c} \cdot \mathbf{C_6H_7}$$

 $\mathbf{R6}) \qquad \mathbf{c} \cdot \mathbf{C}_6 \mathbf{H}_7 \cdot = \mathbf{C}_6 \mathbf{H}_6 + \mathbf{H} \cdot$ 

In a methane flame another potential source of the vinyl radical is hydrogen atom abstraction from ethylene:

$$\mathbf{R1'} \qquad \mathbf{H} \cdot + \mathbf{C}_2 \mathbf{H}_4 = \mathbf{C}_2 \mathbf{H}_3 \cdot + \mathbf{H}_2$$

Cole et al. also propose that  $C_6H_7$  is a key intermediate, but their mechanism postulates

that the reaction of  $C_4H_5$  with actetylene is the dominant formation pathway to  $C_6H_7$ .<sup>13</sup>.

Benzene is formed at temperatures above 1200 K in our methane/air diffusion flame. It is therefore also appropriate to consider reaction sequences which include the ethynyl radical. Colket has proposed that the following sequence of reactions is important above 1500 K:

A variation on this scheme (R7-R10) leads to the polyacetylenes:

R11) 
$$C_4H_3 = C_4H_2 + H$$
  
R12)  $C_4H_2 + C_2H = C_6H_2 + H$ 

A common feature to all of the reaction sequences presented above is the lack of oxygen-containing species in the hydrocarbon growth chemistry. In our flame the concentration of OH radical decreases rapidly on the rich side of the high temperature reaction zone<sup>17</sup>. It is likely that reactive species such as OH· and O· are important in hydrocarbon radical formation reactions and in the oxidation of hydrocarbons in the high temperature reaction zone<sup>10</sup>, but are probably not important in the growth reactions which eventually form aromatic ring compounds.

The mechanisms above may be tested by a comparison of a model's prediction of production rates of key intermediates with the observed production rate of benzene. For a pathway to be viable, the production rate of the intermediate must be at least as large as the net chemical production rate of benzene determined from the experimental data. The proposed mechanisms suggest that the ethynyl radical and the vinyl radical are important intermediates. In order to calculate the production rate of these species it is necessary to know the concentration of hydrogen atoms, which can be estimated from profiles of methyl radical, hydrogen, and methane if the reaction:

$$R13) \qquad CH_4 + H = CH_3 + H_2$$

is equilibrated.

Figure 6 shows the comparison of the observed net production rate for benzene with the maximum production rates of vinyl radical (through reaction R1) and ethynyl radical (through reaction R7) at a height of 9 mm above the burner. The rate of R1 was calculated from the third order rate constant of Payne and



FIG. 6. Comparison of the experimental net chemical production rate of benzene (- $\circ$ -) with the maximum production rates of vinyl radicals (— $\circ$ -, R1') and ethynyl radicals (— $\circ$ , R7) at 9 mm above the burner.

Stief<sup>36</sup>, the measured acetylene concentration<sup>17</sup>, and the hydrogen atom concentration calculated from R13. For the abstraction reaction to form ethynyl radical, R7, the rate constant was computed from the experimental rate constant of the reverse process<sup>37</sup> and the equilibrium constant. For the calculation of the latter, a value of 127 kcal/mol was assumed for the heat of formation of the ethynyl radical<sup>38</sup>.

Figure 6 indicates that the production rate of vinyl radical exceeds the benzene production rate throughout flame regions where benzene is formed. In contrast, the ethynyl radical formation rate via R7 falls far short of the benzene production rate. Since the equilibrium of R7 favors  $C_2H_2$  and H relative to  $C_2H$  and  $H_2$ , the *net* rate of ethynyl radical formation is much lower than that shown in Fig. 6 and can not account for the observed formation of benzene. This result indicates that the production of diacetylene by reactions R7 and R11 represents a parallel hydrocarbon condensation pathway in our flame, one that does not lead to the formation of aromatic rings.

### **VI.** Conclusions

1) Experimental measurements of species concentrations, temperature, and velocity have been used to calculate the net chemical rate of formation and destruction of intermediate hydrocarbons in a methane/air diffusion flame.

2) These results indicate that a significant loss mechanism for acetylene involves surface reactions with particles in regions of the flame where soot inception occurs.

3) Production rate analysis is a promising tool for the evaluation of proposed mechanisms for hydrocarbon growth chemistry. Preliminary results presented here indicate that the vinyl radical is a key intermediate in reaction sequences which lead to aromatic ring formation. Further, diacetylene production represents a parallel condensation pathway and is not involved directly in benzene formation in our methane diffusion flame.

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# **COMMENTS**

A. C. Eckbreth, United Technologies Research Center, USA.: Flames produced on Wolfhard-Parker burners are generally quite fragile and easily perturbed. Have you checked your probe data against any laser measurement techniques to ascertain whether there are any probe-induced profile shifts or distortions?

Author's Reply. We have been concerned with the possibility of flame structure perturbations by the quartz microprobe. Recently the methyl radical, CH3, was detected with both a non-intrusive optical measurement (multiphoton ionization)<sup>1</sup> and in an application of the scavenger probe technique with mass spectrometric detection<sup>2</sup>. When methyl radical profiles from the two measurements are compared, it is seen that the mass spectrometric profile is slightly broadened with respect to the optical measurements, as expected from the larger effective sampling volume diameter for the quartz microprobe. However, there is no significant difference in the location of the maximum CH3 concentration or in the shape of the profile peak, indicating that flame disturbances are small-at least in the region of the flame where the methyl radical comparison can be made.

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M. B. Colket, United Technologies Research Center, USA.: The calculation of production rates for species are dependent strongly on the measured, spatial gradients. If species profiles are broadened due to the sampling process, how much would your calculations of production rates be effected by probe perturbations?

Author's Reply. This is an important question, for which no single answer is appropriate for all circumstances. We have estimated that the quartz microprobe has an effective sampling diameter of  $\sim 0.7$ mm [Ref. 17]. Therefore, the measured concentration profiles are broadened by microprobe sampling, and the peak concentrations are lower than actual flame concentrations. This broadening has a more pronounced effect on production rate calculations for radicals such as CH3, whose spatial distribution is relatively narrow, than for intermediate hydrocarbons such as acetylene and benzene, whose concentrations profiles are broad relative to the effective probe sampling diameter. Calculations have been carried out for acetylene in which the measured concentration profile was broadened by a binomial smoothing function equivalent to a 0.8 mm effective sampling diameter. The additional broadening of the concentration profile leads to a decrease in the acetylene production rate of approximately 10%. The overall uncertainty in the production rate calculations is estimated to be 50%, which includes errors introduced in the calibration and temperature determinations as well as the reproducibility of the experimental measurements. However, these uncertainties do not invalidate the key conclusion made in this paper concerning the importance of vinyl radical chemical growth reactions to the formation of benzene.

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*W. C. Gardiner, University of Texas, USA.* The relative fluxes through vinyl- and ethynyl-based reaction sequences depend strongly upon temperature, and so models that suggest a primary flux through vinyl channels at one position in a flame may also suggest that the ethynyl channels dominate in hotter parts of the same flame. Similar arguments pertain to the effects of H-atom concentrations and fuel structure.<sup>1</sup> Could you please comment on the anticipated range of validity of your conclusion that vinyl pathways dominate.

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Author's Reply. Figure 7 in the text compares the net rate of benzene formation with the maximum forward formation rates of the vinyl and ethynyl radicals. Temperatures in this region of the flame vary from less than 1200 K at a lateral position of 3.0 mm to more than 1900 K at 6.0 mm. The peak temperature at this flame height occurs at a lateral position of 6.6 mm. As Figure 7 illustrates, benzene formation via the ethynyl channel is never fast enough to account for the experimental production rate over this entire temperature range. The dominant role of the vinyl radical in chemical growth reactions indicated by our results is likely to hold for hydrocarbon combustion in general, except perhaps for acetylenic fuels where ethynyl radical concentrations are expected to be high.

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### P. R. Westmoreland, University of Massachusetts, USA.

(1) Your conclusion that  $C_2H_3$  could be an important intermediate in forming benzene is reasonable, although its importance may be in the  $C_4$  formation step. Simple addition of  $C_2H_3$  to acetylenic carbon in a  $C_4$  species gives a linear  $C_6$  radical species that must rearrange before cyclizing.

(2) Your net formation rates (e.g., of  $CH_3$ ) show a small formation peak on the oxidation side. Is this a smoothing artifact, as we observe in similar analysis of flat flames?

#### Author's Reply.

(1) It is not possible for us to identify the dominant C<sub>4</sub> species involved in benzene formation in our methane/air diffusion flame. Our estimates of radical concentrations, other than methyl radical which was experimentally determined, require a high level of confidence that the formation reaction is equilibrated, i.e. the characteristic times for the forward and the reverse chemical reactions are short with respect to the transport times of the reacting species. This proved to be the case in the equilibrium of methyl radicals and molecular hydrogen with methane and atomic hydrogen. Our unpublished calculations suggest that other radical equilibria, such as the abstraction reaction of acetylene by H· to give ethynyl radical and molecular hydrogen, do not meet the characteristic time criteria. Further progress in understanding C4 and C6 chemistry in our flame will depend on a more reliable estimation scheme for polyatomic hydrocarbon radical concentrations or on new quantitative radical concentration measurements.

(2) As you surmise, the extraneous features on the edge of the production rate profiles are smoothing artifacts. Our smoothing routine is based on a cubic Savitsky-Golay filter, which tends to overshoot if there are not enough data points to define a corner in the profile. Hydrocarbon concentrations fall off rapidly to zero at the flame front, and production rate profiles derived from these concentration profiles often exhibit overshoot features in the oxidation region. It is easy to identify such artifacts by varying the number of passes of a profile data set through the filter: smoothing artifacts grow and real features decrease in magnitude with additional passes.

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K. H. Homann, TH. Darmstadt, West Germany. When discussing the vinyl radical as a precursor for benzene, it should not be forgotten that only very little benzene is formed when H-atoms are mixed to acetylene in a discharge flow system at room temperature or a few hundred degrees Celsius. However, the reaction of O-atoms with  $C_2H_2$  produces some benzene. One difference between these two reaction systems is that methylene and methylene-like species  $(CH_2, C_3H_2, ...)$  are formed from O-atom reactions but not from reaction with H-atoms. Thus, one should also consider these species in discussing benzene formation in flames.

Author's Reply. It is difficult to comment on the role of methylene chemistry in the methane/air diffusion flame. Our data suggest a limited role for O atoms in flame regions where hydrocarbon growth chemistry is occurring (see text). If O atoms are important, they are likely to be involved in radical formation reactions close to the high temperature reaction zone. It would be interesting to compare an estimate of the rate of methylene formation at the flame front with the observed benzene formation rate as we have done for the vinyl and ethynyl radicals. Unfortunately, quantitative O-atom concentration profiles are not yet available for any hydrocarbon diffusion flame nor can estimates be made with confidence.