FORMATION OF HIGH MOLECULAR WEIGHT AROMATICS IN FUEL-RICH FLAMES

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GENERAL OBSERVATIONS

Gas composition measurements as a function of distance or time through the reaction zone of fuel-rich premixed flames reveals the occurrence of high molecular weight aromatics formed by growth reactions that accompany the destruction of the fuel. The lumped concentration profile of all species heavier than molecular weight M exhibits a sharp peak (Fig. 1) indicative of net production of heavy material giving way to net consumption during passage through the reaction zone of the flame (from left to right in the figure). The data in Fig. 1 were obtained by probing along the centerline of a low-pressure, one-dimensional or plug-flow premixed acetylene-oxygen flame using a molecular-beam forming sampling instrument with on-line mass spectrometry. The heavy aromatics at flame temperatures, here about 1800 K, include both ions and neutrals. The heavy ions profile in Fig. 1, obtained (1) with a Faraday cage and electrical deflection of the molecular beam in the sampling instrument (2), includes ions larger than about 300 amu. The profile for M > 1000 amu species, obtained (3) with an on-line quadrupole mass spectrometer in the sampling instrument (Fig. 2), includes both ions and neutrals. The reactions involved are rapid, 3 mm of distance in Fig. 2 corresponding to a time interval of about 1 ms. When the fuel equivalence ratio [ϕ = (fuel/oxygen)/(fuel/oxygen) stoichiometric] is above the critical value for soot formation, it is at the location of the peak concentration of the heavy aromatic compounds that the soot particles begin to form (4). When soot formation is impending, an increase of fuel/oxygen ratio by only a few percent gives a 100-fold increase in the peak concentration of the heavy aromatics.

RESOLUTION OF MOLECULAR WEIGHT GROWTH

In order to gain more understanding of the evolution of heavy hydrocarbons, mass spectrometer intensity profiles such as that for $I_{M>1000}$ in Fig. 1 but with the cutoff mass M varied in 50 amu steps from 200 amu to 750 amu were measured in a near-sooting low-pressure (2.67 kPa) C_6H_6/O_2 flame (4,5). If $I_{M>1000}$ is the signal intensity of all species of molecular weight M greater than the cutoff value m, then a probability distribution function (p.d.f.) $f_{200}(m)$ can be defined as

$$f_{200}(m) = -d[I_{M>m}/I_{M>200}]/dm$$

where $f_{200}(m)$ represents the number fraction of all species greater than 200 amu lying in the range m to m + dm.

The p.d.f.'s for five distances from the burner (5) are shown in Fig. 3. The p.d.f. at 7.95 mm is heavily weighted toward the mass range 200-300 amu. As the distance from the burner increases, the p.d.f. increases at the higher masses and decreases at the lower masses. At distances above 10.0 mm, the signal between 200 and 300 amu is a small to negligible fraction of the total, and the distributions are relatively uniform in the range 300-600 amu. At 10.9 and 12.1 mm, the distributions turn upward at the far right indicative of a faster growth of the higher-mass species, but it is not known if this apparent behavior is real or an artifact of the data at this high-mass extreme of the mass range studied.

These observations show that although the number density of high molecular weight species decreases with distance from the burner beyond the location of the

maximum concentration (e.g., Fig. 1), the mean molecular weight continually increases. In order to determine how the total mass of heavy species changes as the number decreases, the p.d.f. has been multiplied by m to convert to a mass basis and by

$$I_{M>200}/(I_{M>200})_{z=7.95mm}$$

to normalize the mass with the constant number of moles of heavy material existing at an arbitrarily fixed distance (z = 7.95 mm) from the burner. The resulting function,

$$mf_{200}(m)I_{M>200}/(I_{M>200})_{z=7.95mm}$$

is shown in Fig. 4 for different molecular weights as a function of distance from the burner (5). A point on one of the curves represents the mass of species of the indicated molecular weight existing at the indicated distance from the burner, expressed as a ratio to the total number of moles of M>200 amu material existing at 7.95 mm.

It can be seen in Fig. 4 that the mass of material at a given molecular weight exhibits a peak at a height above burner which increases with increasing mass number. The shapes of the curves and the location of the peaks are the same as would be seen if number of moles instead of mass were plotted, since the number curves could be produced by vertical displacement of each mass curve in accordance with division by the constant molecular weight indicated thereon. In comparison with mole fraction profiles for individually identified species of m less than or equal to 200 amu, shown later, the curves in Fig. 4 constitute a continuation of the progression seen for the individual hydrocarbon species, namely molar concentration profiles peaking as m increases. Figure 4 shows that the peak concentrations also decrease as m increases. The mean molecular weight and overall mass and number concentrations of the high-mass material (5) are shown in Fig. 5.

INTERPRETED GROWTH BEHAVIOR

The above information shows that the rapid decrease in number concentration of heavy species that occurs immediately downstream of the peak concentration (Fig. 1) is not only accompanied by increasing mean molecular weight but also a net consumption or loss of material. Whether this consumption is due to oxidation, pyrolysis, or a combination of these has been addressed (5) by calculation of fluxes of O_2 and hydrocarbon species at the beginning and end of the zone of the heavy species consumption, both for the above near-sooting flame data and for similar data from a sooting C_6H_6/O_2 flame operated under otherwise identical conditions. The fraction of the initial oxygen remaining as O_2 at the beginning of the zone of rapid consumption of M>700 amu material is 37.2% and 18.3% for the near-sooting and sooting flames, respectively, and the O_2 remaining at the end of the zone of rapid consumption of M>700 amu material is about 1% of the initial value in both flames. Therefore the amount of oxidation occurring within this zone is indeed substantial, thus allowing the possibility that oxidation plays a role in the destruction of the high-mass material or its pyrolytic decomposition products. It is also found that the amount of M>700 amu material increases by a factor of 100 in going from the nearly sooting to the sooting case, even though the benzene fed is only increased by about 10%. In addition, the benzene fuel is almost gone when the M>700 material reaches its maximum concentration, indicating that the amount of these heavy species continues to increase as long as benzene is available. This behavior may mean that the concentration of oxidizing radicals that consume heavy species is suppressed by reaction with benzene, and also that benzene serves as a source of growth species for the heavy material. When the heavy species are undergoing rapid consumption, an even larger quantity of the prevalent intermediate, acetylene, is being consumed. Consequently, with regard to the molecular weight growth that accompanies the destruction of heavy compounds, acetylene and related species such as diacetylene (C_4H_2) and vinylacetylene (C_4H_4) may be important reactants.

IDENTIFIED SPECIES

Species and reactions involved in the early stages of the formation of high molecular weight compounds were studied (3,4) in the near-sooting C_6H_6/O_2 flame discussed above using the instrument shown in Fig. 2. Measured mole fraction profiles from which species fluxes and net reaction rates were computed are presented in Figs. 6-10. It will be noted in these figures that numerous intermediates are involved whose formation and subsequent destruction exhibit a general trend to larger molecular weights and smaller peak concentrations. It is this progression or sequential growth that is mentioned above as continuing on to the high molecular weight species. This behavior in both the near-sooting C_6H_6/O_2 flame and the sooting C_2H_2/O_2 flame discussed above is illustrated in Fig. 11 where the mole fractions of selected compounds are plotted with the intensities of heavy species. The growth proceeds on to soot if the fuel/oxygen ratio exceeds the critical soot limit.

MECHANISTIC FEATURES OF AROMATICS GROWTH

Analysis of these data has provided some insights into possible mechanisms of destruction of the fuel and the formation and destruction of intermediates (3,4,6). There is indication that aromatic hydrocarbons provide a structure capable of stabilizing, by internal aromatic substitution reactions, the radicals formed from addition of aromatic radical species to non-aromatics. Specifically, it appears that the combined presence of aromatic radicals, unsaturated aliphatics such as acetylenic species and H atoms is particularly favorable to growth of PAH and soot. Therefore, the production of phenyl radical (C_6H_5) and the competition between its destruction, especially with O_2, and addition to unsaturated aliphatics are important factors in the molecular weight growth of aromatics.

With these mechanistic points in mind we return to the earlier discussion of the consumption of species immediately downstream of the peak concentration of the high molecular weight material. While the consumption is mainly by oxidation, it is accompanied by further increase in the mean molecular weight of the heavy species. Since the largest amount of material being consumed is acetylene, diacetylene, and vinylacetylene, and since these unsaturated aliphatics are identified as important species for molecular weight growth by addition reactions with aromatic radicals, one can infer that the acetylenic species do indeed contribute to the growth of the aromatic structures of which the heavy molecules and soot are comprised, presumably by addition reactions with the heavy aromatics. Aromatic species with acetylenic side groups are observed in the mass range ($\gtrsim$200 amu) where individual identifications were possible, and the amount of acetylenic species consumed in this region of the flame greatly exceeds the amount of soot eventually formed. However, the peak flux of heavy species also exceeds the amount of soot eventually formed, so the proportions of the final soot mass contributed by the acetylenic species and by the heavy aromatics are not established. Qualitatively similar behavior was observed in a sooting acetylene/oxygen flame. In both the acetylene and benzene flames, the oxidative and possibly pyrolytic destruction of heavy species occurring downstream of their peak concentration would appear to be an important source of polycyclic aromatics emitted from the flame.

FORMATION OF FIRST AROMATIC RINGS

In flames of aliphatic fuels the first aromatic rings must be formed from non-aromatic precursors. Possible mechanisms for this critical step have been assessed (7) by comparing predicted formation rates against experimental values calculated from mole fraction profiles of compounds measured in a low-pressure 1,3-butadiene/oxygen flame using the instrument shown in Fig. 2. Postulated mechanisms involving butadienyl radical (C_4H_5) reacting with an acetylenic species and followed by rapid

cyclization were found to form benzene, toluene, phenylacetylene, and styrene at rates consistent with the data. The rate-controlling steps and predicted rate constants are as follows:

$$C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H, \quad \log k_1 = 8.5 - 3.7/\theta$$
$$C_4H_5 + C_3H_4 \rightarrow C_6H_5CH_3 + H \quad \log k_2 = 8.5 - 3.7/\theta$$
$$C_4H_5 + C_4H_2 \rightarrow C_6H_5C_2H + H, \quad \log k_3 = 8.5 - 1.8/\theta$$
$$C_4H_5 + C_4H_4 \rightarrow C_6H_5C_2H_3 + H, \quad \log k_4 = 8.5 - 0.6/\theta$$

where k's are in $\ell\ mol^{-1}s^{-1}$ and $\theta = 2.3\ RT$ is in kcal mol^{-1}. Aromatics thus formed could subsequently participate in molecular weight growth as discussed above.

CONCLUSIONS

The chemistry of heavy aromatic compounds in fuel-rich flames involves numerous intermediate species whose sequential formation and destruction give a progression to decreasing amounts of increasingly heavy species, leading eventually to soot if the fuel/oxygen ratio is high enough. The combined presence of aromatic radicals, unsaturated aliphatics such as acetylenic species and H atoms is particularly favorable to molecular weight growth. When the initial fuel contains no aromatics, mechanisms controlled by butadienyl radical reacting with acetylenic species can form single-ring aromatics at rates consistent with observed values.

ACKNOWLEDGEMENTS

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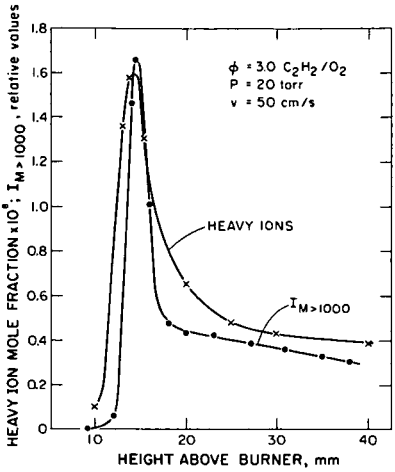


FIGURE 1. Concentration of heavy ions and signal intensity of high-mass (M>1000 amu) species in sooting acetylene-oxygen flame (ϕ = equivalence ratio; P = pressure; v = cold gas velocity).

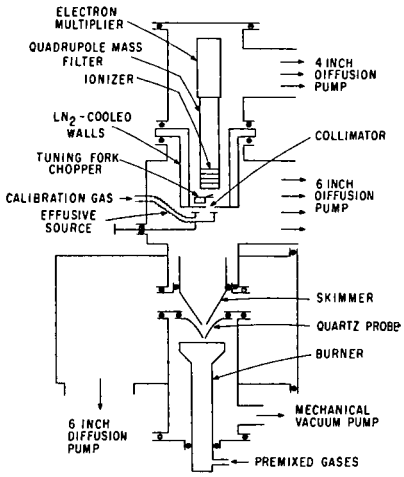
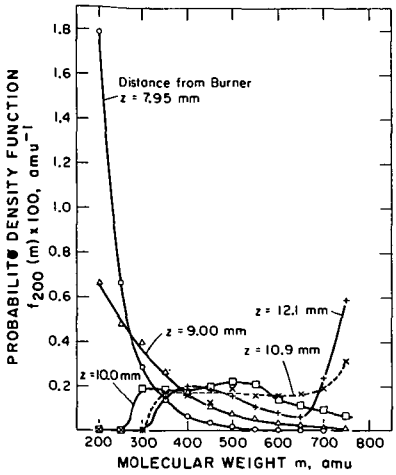
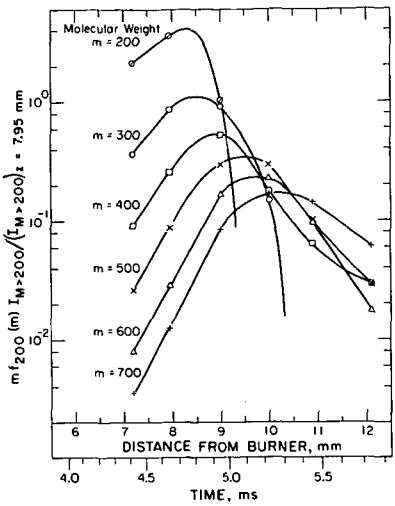


FIGURE 2. Molecular beam mass spectrometer system for the study of one-dimensional low-pressure premixed laminar flames.





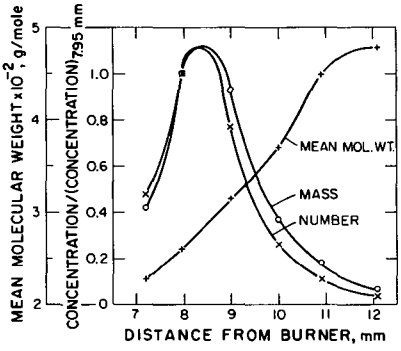
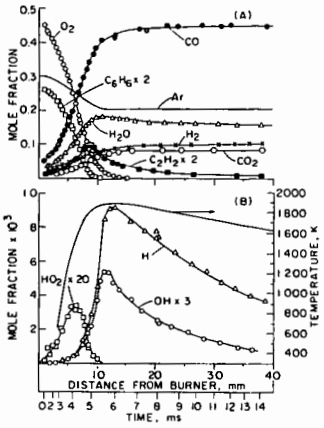


FIGURE 3. (ABOVE, LEFT) Probability density function for high-mass signal at several positions in near-sooting benzene-oxygen flame. (Pressure = 2.67 kPa; cold gas velocity = 50 cm/s; equivalence ratio = 1.8.)

FIGURE 4. (ABOVE, RIGHT) Variation with distance from burner of mass of material in molecular weight range m to m + dm at different molecular weights, normalized with number of moles of M>200 amu material at 7.95mm above burner. (Same flame as in Fig. 3.)

FIGURE 5. (BELOW) Variation of mean molecular weight and mass and number concentration of M>200 amu material with distance from burner. (Same flame as in Fig. 3.)



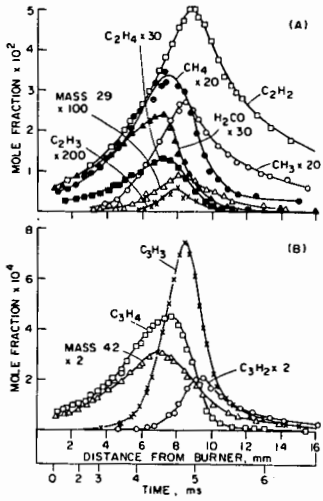
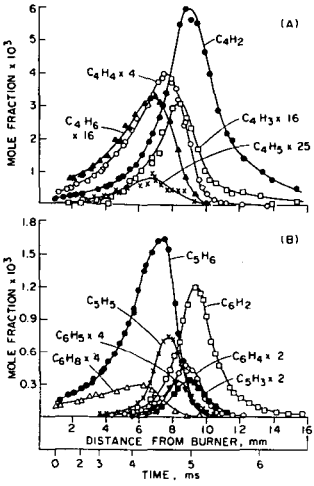


FIGURE 6. (LEFT) Mole fractions and temperature vs. distance from burner in near-sooting benzene-oxygen flame. (Same flame as in Fig. 3.)

FIGURE 7. (RIGHT) Mole fractions of species with masses between 15 and 44 amu vs. distance from burner in near-sooting benzene-oxygen flame. (A) Mass 29 may be C_2H_5 or HCO. (B) Mass 42 may be C_3H_6 or C_2H_2O. (Same flame as in Fig. 3.)



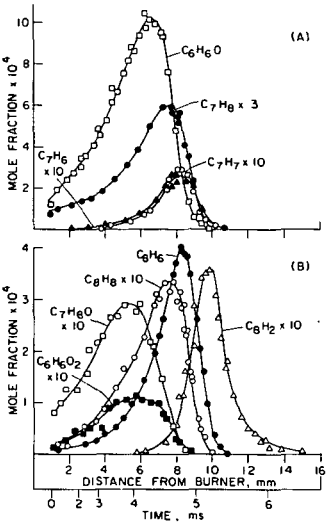
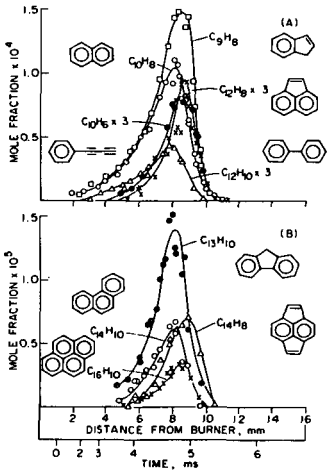


FIGURE 8. (LEFT) Mole fractions of C_4 (A), C_5 and C_6 (B) hydrocarbons vs. distance from burner in near-sooting benzene-oxygen flame. (Same flame as in Fig. 3.)

FIGURE 9. (RIGHT) Mole fractions of species with masses between 90 and 100 amu vs. distance from burner in near-sooting benzene-oxygen flame. (Same flame as in Fig. 3.)



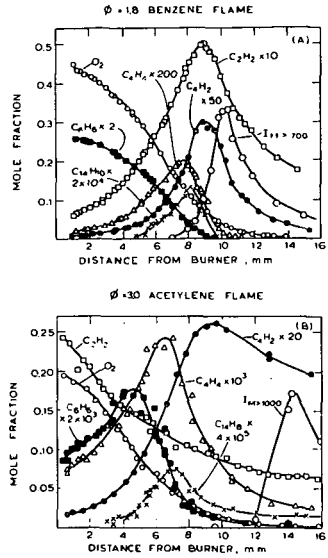


FIGURE 10. (LEFT) Mole fractions of polycyclic aromatic hydrocarbons vs. distance from burner in a near-sooting benzene-oxygen flame. (Same flame as in Fig. 3.)

FIGURE 11. (RIGHT) Mole-fraction profiles of selected compounds and signal intensity profiles of high molecular weight species for benzene-oxygen (above) and acetylene-oxygen (below) flames. [Same flames as in Fig. 3 (above) and Fig. 1 (below).]