ARE IONS IMPORTANT IN SOOT FORMATION?

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I. INTRODUCTION

Many chemical mechanisms have been proposed for the formation of incipient soot in flames. The ionic mechanism has not been widely embraced; it is considered a competitor to free radical mechanisms which have received more attention. It seems timely to review the evidence for the ionic mechanism, which we do here.

The precursor of soot formation is assumed to be the propargyl ion, $C_3H_3^+$ (1-3). The source of this ion is not clear but it is the dominate ion in fuel rich hydrocarbon flames and is generally considered to be a primary chemi-ion, i.e., derived from the reaction of neutral species. There are two isomers of $C_3H_3^+$, a linear structure and a more stable cyclic structure. Measurements of reaction rates for these two isomers at near room temperature demonstrate that reactions of the linear isomer are fast, generally equal to the Langevin rate, while reactions of the cyclic isomer are slower (4-6). Eyler and associates (7) have recently determined that the rate of linear $C_3H_3^+$ reacting with acetylene is small compared to Langevin theory (8,9). The validity of extrapolating these measurements to high temperatures is not clear. The Langevin theory, for ions reacting with non-dipolar molecules, does not predict a temperature dependence. Which isomer of $C_3H_3^+$ is formed initially in flames is also not known, nor is the rate of isomerization.

In the ionic soot formation mechanism, the precursor ion reacts with neutral species, e.g., acetylenes, to produce larger ions. These larger ions continue to react further to produce ever increasingly larger ions.

A major feature of this mechanism is the large rate coefficients for ionmolecule reactions and the ease with which ions isomerize (8). The formation of a cyclic structure does not represent a significant energy barrier as it does for a free radical mechanism. Some of the electrons produced in the chemi-ionization reaction produce negative ions by electron attachment to large molecules; these reactions are favored by low temperature and increasing molecular weight of the neutral reactant. As the ions grow larger their recombination rate coefficient for reaction with electrons or negative ions increases, so positive ions are removed, forming large neutral molecules, the equivalent of small neutral soot particles. The small neutral particles continue to grow and as they become larger their work function approaches that of bulk graphite. At sufficiently high temperature, these particles become thermally ionized; these thermally ionized particles are not of interest for soot nucleation.

In this paper we review the evidence for the sequence of reactions starting with $C_3H_3^+$ and proceeding through large soot ions; this sequence of reactions has been labeled "the ionic mechanism."

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II. EVIDENCE

A. <u>Concentration</u>

Concentrations of ions have been measured by AeroChem (2,3,10), Delfau and associates (11,12), and Homann and associates (13,14) in what has been referred to as the "standard flame." This is a premixed, sooting acetylene/oxygen flame on a flat flame burner at 2.7 kPa, an equivalence ratio of 3.0, and an unburned gas velocity of 50 cm/s. Ion concentrations are shown in Fig. 1 along with neutral soot concentrations, charged soot concentrations, and the flame temperature. The ion concentration in this flame is sufficient to account for the formation of the observed soot.

B. <u>Reaction Rates</u>

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Ion-molecule rate coefficients are generally several orders of magnitude greater than for neutral species reactions (8), which, of course, means that the concentration of ions does not have to be as great to react at the same rate.

Figure 1 also contains evidence that the rates of ion-molecule reactions are sufficiently rapid in flames to account for soot formation. As the ion concentration decays by ion recombination, the soot concentration increases. The slopes are comparable within the accuracy of the data. We note, however, that soot particles are identified as those which can be detected using an electron microscope, i.e., their diameter exceeds 1.5 mm.

Several available sets of data on neutral soot particle diameters and positively charged soot particle diameters are presented in Fig. 2 for the standard C_2H_2/O_2 flame. These data have presented a dilemma (15); it appears that neutral particles grow faster than charged particles, but in the early part of the flame the charged particles have a larger diameter. This question seems to relate more to particle growth and thermal ionization than to soot nucleation; nevertheless the location of the phenomena in the flame is at just the distance where the initial ion concentration is falling and the concentrations of neutral particles and charged particles are increasing. In previous calculations (1,16) of thermal ionization of soot particles about 2 cm downstream from the burner, the assumption was made that equilibrium was approached from the side of excess neutral particles. This is difficult to rationalize if the concentration of charged particles exceeds the concentration of neutral particles at small distances where the particle diameters.

The fraction of thermally ionized particles and the rate of thermal ionization are both very sensitive to particle diameter. For the small neutral particles the calculated ionization rate is slow compared to the experimental rate. Thus at 2.25 cm above the burner, with the Richardson equation modified for small particles (17), we calculate a rate of ionization of 2×10^{11} charged particles/(cm³ s) and we measure a rate of 6×10^{11} charged particles/(cm³ s) from the slope of the "charged soot" curve in Fig. 1. Between 2.5 and 3.0 cm the calculated rate exceeds the observed rate; here and at greater distances equilibrium controls the concentrations. Thus at the first appearance of soot the rate of thermal ionization of neutral particles is too small to account for the observed rate of charged particle appearance; close to the burner equilibrium is approached from the direction of excess charged particles. This is further evidence that charged species are involved in the formation of soot.

The difference in slopes of the neutral and charged particle concentrations in Fig. 2 is probably due to a faster rate of ion-electron recombination for large ions than for small ions. For example, increasing the particle diameter from 5 to 10 nm increases the rate coefficient of recombination from about 1.3×10^{-5} to about 3.8×10^{-5} cm³/s. Thus the larger charged particles disappear more rapidly than the smaller ones. In the region of the flame where this occurs, the observed charged particles are derived from the chemi-ions produced early in the flame and are not derived from the neutral particles. This is not only further evidence for the ionic mechanism of soot formation, but it makes very awkward any explanation of the source of ions being the thermally ionized particles as some have suggested.

C. <u>Confirmation of Ions</u>

All of the individual ions involved in the postulated mechanism, up to mass 557, have been observed in sooting flames (2,3,11,12). The confirmation that ions larger than these are present in the flame, prior to the appearance of soot, has also been documented (13,14).

D. Location of Ions in Flame

The order of appearance of ions and soot, Fig. 1, in a flame is not in itself evidence that ions are produced before soot in the reaction sequence; the order of appearance would be reversed if the rate of production of soot from ions were fast compared to the rate of production of ions. However, when the species peak at considerable distance apart in the flame it seems safe to assume that the first peak precedes the second in the reaction sequence as well as in order of appearance. This assumption is further warranted when there is no clear means of proceeding from soot to ions (10). With these caveats, the appearance of ions in the flame with respect to the appearance of soot is evidence for ions being the precursors of soot.

Further evidence of a similar nature comes from observations in diffusion flames at one atmosphere. We have made ion concentration measurements (19) in the same methane/air flame on which Smyth et al. (20) made a number of measurements. Our temperature profiles agreed with theirs. The data for this diffusion flame are summarized in Fig. 3 and the rationale for the estimates of concentrations are summarized in the caption. The soot concentration profile was not measured by Smyth et al., but the position of the soot maximum in the flame was determined by laser induced ionization. The relative concentrations of polycyclic aromatic hydrocarbons, PCAH, were estimated from laser induced fluorescence. We confirmed the radial location of the soot maximum by laser extinction measurements at a wavelength of 633 nm somewhat higher in the flame. We estimate from our measurements that the volume fraction of soot is about 5×10^{-6} , which for 20 nm diameter particles would correspond to about 10^{10} particles/cm².

The location of soot, Fig. 3, with respect to the possible reactants is evidence for the ionic mechanism as opposed to a mechanism involving only acetylene and a PCAH. For a reaction of acetylene and PCAH to be to be reasonable, it is necessary to assume something else is involved, such as hydrogen atoms (21,22), or that the rate limiting reaction has a very high activation energy. The soot is located between the peak concentrations of acetylenes and ions, just where it would be anticipated if these were the two reactants producing it.

An important question with respect to soot formation is "why does inception stop?" (23). Harris has recently suggested that the falloff in oxygen concentration may be responsible due to its promotion of the formation of high energy species which are important for soot formation and which disappear along with the oxygen. He suggested that the production of excess H-atoms is possibly responsible for the effect. An even more obvious explanation for the termination of soot inception would be the termination of ion formation and the rapid decrease in ion concentration, see e.g., Fig. 1. It is a long established fact that ions show a sharp peak in the flame front of hydrocarbon flames (24,25).

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E. Changes With Equivalence Ratio

In premixed flames dramatic changes in ion concentrations occur at the threshold fuel concentration for soot formation as shown in Fig. 4. Small flamme ions are replaced by large ions as the equivalence ratio is increased through the threshold soot point. This simple observation would be consistent with an ionic

mechanism of soot formation; there are, however, complications. Why does the total concentration of ions increase at higher equivalence ratios beyond the soot threshold? This observation has, in fact, been used to argue against the ionic mechanism; namely that the occurrence of the increase in ion concentration with equivalence ratio was due to ionization of charged particles (11,15). We have subsequently demonstrated that thermal ionization of soot particles cannot be the explanation for this increase (10) but the phenomenon remains unexplained. Both the maximum flame temperature (26) and the total ion recombination coefficient (10) change at the soot threshold concentration. The temperature drop is probably due to ionicease.

F. Fuel Effects

The occurrence of ions and the appearance of soot in flames of various fuels are consistent with the ionic mechanism of soot formation, i.e., fuels which do not produce ions do not produce soot (1).

Another indication of a correlation between fuel effects on soot formation and ionization can be gleaned from the correlation made by Takahashi and Glassman (27) between the equivalence ratio for soot formation and the number of carbon bonds; the tendency to soot increases with the number of carbon bonds. This is similar to the tendency of compounds to produce ions under various conditions. In flame ionization detectors for gas chromatography the magnitude of the signal produced correlates with the number of carbon atoms in the molecule (28). In premixed fuel/oxygen flames, Bulewicz and Padley (29) found that the electron current increased with the number of carbon atoms in the molecule. Interestingly acetylene differed from their correlation as it does in the Takahashi and Glassman correlation.

G. <u>Chemical Additive Effects</u>

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Some of the first evidence quoted for an ionic mechanism of soot formation was from observations of the effect on soot formation of chemical additives with low ionization potentials. Strong correlations are observed between the effectiveness of additives on soot formation and their ionization potentials (30). Alkaline earths are a special case because the level of ionization is greater than anticipated by thermal equilibrium; ions are produced by chemi-ionization (31).

The same additives have been observed to both promote or inhibit (30) the formation of soot, and the results have been interpreted as affecting either the nucleation or the coagulation step. Much of the confusion arises because of the number of possible roles an additive can play and the fact that these roles can vary with the experimental conditions, e.g., the concentration of the additive (32).

The effects of additives on soot nucleation are based on two processes as suggested by Addecutt and Nutt (33): (1) the transfer of charge from a chemi-ion to a metallic atom, A, (34) e.g.:

where H^+ is any hydrocarbon ion, such as C₃H₃+, or (2) by increasing the concentration of electrons due to thermal ionization of easily ionized metals. This would increase the rate of dissociative recombination of chemi-ions:

M+ + e- + Products 3)

Either one of these mechanisms would remove the precursor chem-ion from the system and thus reduce the number of soot nuclei produced. Reaction 1 will be important under conditions such that the equilibrium concentration of H^+ is lower than that of A^+ . In fact, the rate coefficient for Reaction 1 is so much greater than for Reaction 2 that equilibrium concentrations of A^+ may be approached via Reaction 1 rather than Reaction 2. The metal ion, A^+ , may also be produced in greater than equilibrium concentrations by Reaction 1 (35). Thus the specific mechanism by which the addition is effective will be determined by the relative equilibrium concentration of A^+ to H^+ and the time available to approach equilibrium.

Miller (36), in a study of additive effects on flame quenching, observed that the addition of carbon tetrachloride to a spherical low pressure diffusion flame transformed a nonsooting flame to a sooting flame and simultaneously completely altered the ionic composition of the flame. The chlorine from the additive forms compounds which attach electrons producing large concentrations of negative ions. These reduce the rate of recombination of positive ions because recombination coefficients with negative ions are about 100 times smaller than with electrons. Thus the positive ion concentration is increased, and this increase, via the ionic mechanism of soot formation, produces observable soot.

Bulewicz et al. (32) have studied the effect of metal additives on soot formation in flames and have given a detailed interpretation of their results which is in complete accord with our current concepts of the mechanism of soot formation via an ionic mechanism. A number of chemical additives were added to the fuel side of an acetylene/oxygen diffusion flame. The soot was collected on a glass fiber filter and weighed. The soot particle size was determined by electron microscopy of samples taken at 2 cm, about 1 ms, above the burner rim, and the total positive ion concentration was determined by Langmuir probe. Flame temperatures were in the range of 1400 to 1800 K.

The same additive acted as a pro-soot or an anti-soot additive, depending upon the total ion concentration due to the additive. With increasing ion concentration, the total quantity of soot increases and then decreases so that at one specific additive concentration, the amount of soot is the same as without the additive. At this additive concentration the particle number density reaches a maximum. Beyond this concentration the number density, total mass of soot, and the soot particle size all decrease so that the dominant effect of the additive is on the nucleation rather than the coagulation, see e.g., Haynes et al. (37).

Bulewicz et al. (32) explain both the pro-soot and the anti-soot effects by means of an ionic mechanism. The reader is referred to their paper for the detailed arguments. Briefly, the anti-soot effect is due to charge transfer from the precursor hydrocarbon ion, N⁺, to the metal atom as in Reaction 1. They point out that in their flame, thermal ionization of the metal atom would be too slow to produce electrons above the natural flame level so that Reaction 3 cannot be effective in reducing the concentration of hydrocarbon flame ions. The pro-soot effect is explained by demonstrating that small concentrations of additive may, in fact, maintain the level of H+ at a higher value throughout the flame than when no additive is present. The potassium level in the range of concentration near the crossover point from pro-sooting to anti-sooting varies from about 1010 to 1014 atom/cm³. At about 1600 K, the equilibrium concentration of K+ varies from about 10⁸ to 10¹⁰ ion/cm³ (function of solution molarity). The natural flame ionization concentration is about 1010 ion/cm3, several orders of magnitude above equilibrium levels. When the concentration of K is 1014 and the concentration of M+ is 1010 it is clear that Reaction 1 can proceed at a significant rate, thus reducing the concentration of M⁺. At this high level of additive concentration the equilibrium

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concentration of K⁺ cannot be exceeded. On the other hand when the K concentration is only 10^{10} atom/cm³, the H⁺ concentration can be only negligibly reduced in the time available. However, the equilibrium level of K⁺, which is only about 10^8 ion/cm³, may be significantly exceeded because the recombination rate is slow compared to the rate of charge transfer from chemi-ions, Reaction 1 (see e.g., Ref. 35). Farther downstream the slow decay of K⁺ maintains a higher level of total ionizations and at this point Bulewicz et al. (32) suggest that the reverse of Reaction 1 maintains the concentrations of H⁺. In the absence of this reaction, H⁺ would have decayed because dissociative recombination of molecular ions is about two orders of magnitude greater than for atomic ions which must decay by a three body process. Thus new ionic nuclei are available at later stages in the combustion process to grow to incipient soot particles.

The pro-soot action of higher ionization elements, e.g., Pb 7.42 eV; Mg 7.64 eV; Cr 6.76 eV; Co 7.66 eV; Mn 7.43 eV; and even Li 5.39 eV, are explained by the above argument. Their equilibrium ionization levels are very low and their ionization potentials are somewhat less than those for hydrocarbon ions, so a concentration above the equilibrium concentration is expected. Clearly this analysis merits more detailed modeling in which all of the simultaneous reactions can be accounted for more quantitatively. It does, however, at this stage of development, support the ionic mechanism of soot formation.

III. SUMMARY

The answer to the question raised in the title seems to be "yes."

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FIGURE 1 COMPARISON OF TOTAL ION CONCENTRATION AND SOOT CONCENTRATION PROFILES IN LOW PRESSURE (2.67 kPa), \emptyset = 3.0 ACETYLENE/OXYGEN FLAME (50 cm/s UNBURNED GAS VELOCITY) The temperature, ion profiles, and time axis are from AeroChem (10). The soot profiles are from Howard et al. (38) and have been reduced by 50% so the charged soot and ion concentrations

agree at 3.5 cm (10).





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FIGURE 3 PROFILES 15 mm ABOVE A WOLFHARD PARKER SLOT BURNER SUPPORTING AN ATMOSPHERIC PRESSURE METHANE/AIR DIFFUSION FLAME

Fuel velocity = 9.7 cm/s. Air velocity = 19.4 cm/s. TEMPERATURE and positive IONS (concentration measured with Langmuir probe, 1000 amu ion mass assumed) profiles measured at AeroChem (19). Other profiles from Smyth et al. (20). Profile for C4H2 represents experimental profiles at 9 mm scaled to 15 mm by the acetylene ratio at the two heights. PCAH is visible laser induced fluorescence profile approximately scaled with a constant factor based on the ratio of $C_{14}H_{5}$ to C4H6 concentrations in the low pressure flame of Figs. I and 2. SOOT is in arbitrary units and was scaled to maximize at the same concentration as IONS.



FIGURE 4 VARIATION OF MAXIMUM ION CONCENTRATION WITH EQUIVALENCE RATIO IN LOW PRESSURE ACETYLENE/OXYGEN FLAME TOTAL IONS are Langmuir probe measurements. Profiles of individual ions indicated by mass in amu were measured with flame ion sampling mass spectrometry. The ratio of TOTAL IONS to the sum of the individual currents at $\emptyset = 3$, where mass 39 dominates (+) provided a calibration of the mass spectrometer for lighter masses. Similarly, > 300, representing all heavy masses between 300 amu and the high mass cut-off of the mass spectrometer, was put on an absolute scale at $\emptyset = 2.9$ (+). Shading indicates the threshold for soot formation.