

THE ROLE OF IONS IN SOOT AND DIAMOND FORMATION

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INTRODUCTION

Soot and diamonds are different forms of carbon. It is thus natural to examine mechanisms which have been proposed for the formation of soot with respect to the mechanism of diamond film deposition. Frenklach and Spear have done this with respect to the free radical mechanism of soot formation (1). Diamond deposition is frequently a plasma process and ions have been proposed in several mechanisms to explain the process. There is considerable evidence (2) of an ionic mechanism of soot formation. The demonstration that diamonds can be deposited from combustion flames (3, 4) also makes it timely to consider soot forming processes in flames as they might relate to diamond deposition. Thus we briefly review the ionic mechanism of soot formation and the evidence for an ionic role in diamond deposition; we then make a few observations relevant to the role of ions in the mechanism of diamond deposition.

IONS IN SOOT FORMATION

The ionic mechanism of soot formation, Figure 1, postulates that chemiions, HCO^+ and C_3H_3^+ , which are present in excess of equilibrium in hydrocarbon flames, rapidly grow by ion-molecule reactions in which several neutral species continue to add to an increasingly larger ion. As an ion becomes larger, it is neutralized by the electrons produced in the chemiionization reactions. This process gives both charged and neutral incipient soot particles which continue to grow by the addition of acetylene and other small neutral species. There are two important considerations in the ionic mechanism: (1) the large rate coefficients for ion-molecule reactions, and (2) the rapid isomerization of ions to produce a cyclic structure. Formation of the first ring is the main problem with the neutral mechanism and has absorbed much of the research attention relevant to the neutral mechanism.

The soot concentration, in many flames, is in excess of equilibrium so must be driven by a species whose concentration exceeds equilibrium. Chemiionization is a nonequilibrium process producing ionic concentrations orders of magnitude in excess of equilibrium.

In Figure 1, the direct path to C_3H_3^+ appears unimportant in flames (5) but may be important in pyrolysis systems producing soot, where ions are also observed (6). Therefore C_3H_3^+ is probably generated by a series of ion-molecule reactions from HCO^+ . The ion C_3H_3^+ grows by adding small neutral species in a series of ion-molecule reactions, in which any one of the growth species, see, e.g., Figure 1, may add to a given ion to produce a larger ion. At each stage the ion may also be neutralized by reaction with an electron produced in the initial chemiionization step. The product of this reaction, usually a dissociative recombination, is identified in Figure 1 as "neutral reactant" (e.g., a polycyclic aromatic hydrocarbon) and this neutral species may continue to grow by a neutral free radical mechanism, also leading to an incipient soot particle.

All of the ions proposed in the ionic mechanism have been observed in flames up to mass 557 amu; the concentration of ions has been demonstrated experimentally to be sufficient to account for the concentration of soot measured; and the rates of ion formation in both premixed (7) and diffusion (2) flames are about the same order of magnitude as the rate of soot formation.

IONS IN DIAMOND FORMATION

Diamond films have been deposited by many different techniques including electrical discharge systems, e.g., microwave, rf, and dc glows; dc and rf arcs; and arc jets. They have also been made with ion beams, combustion flames, and hot filaments. The electrical discharge systems are based upon electrically driven plasmas. From the above discussion, it is clear that the combustion system is also a plasma. This leaves only the hot filament technique as not obviously involving a plasma.

It has been demonstrated, however, that in the hot filament technique, the application of an electric field to the substrate can influence the rate of diamond film deposition. Yarbrough (8), e.g., found that a positive voltage on the substrate increased the rate of diamond deposition and a negative voltage prevented deposition. This indicates the importance of charged species in the deposition process and puts this system as well in the plasma category. The source of the ionization is most likely electron emission from the hot filaments which were tantalum tubes heated to 2370 to 2470 K (9). Thus all diamond preparation systems have a unifying feature--the presence of ions.

In a magneto-microwave plasma, Susuki et al. (10) also observed the rate of film deposition to be accelerated by application of a positive electric field to the substrate. In these two systems, observations indicate either diamond deposition enhancement by negative ions or electrons, or an inhibiting effect by positive ions.

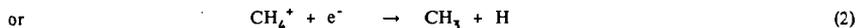
On the other hand, others have found that accelerating positive ions toward the substrate surface enhances the rate of diamond deposition (11), or more generally the application of a negative bias to the substrate increases the rate of film deposition or alters the properties of diamond (12) or diamond-like (13) films.

MECHANISTIC IMPLICATIONS

Since a plasma generated by an electric field is a common component of many diamond film deposition processes, we examine the process of creation of active species in an electrical discharge device. Most deposition processes use a mixture of hydrogen containing a few percent methane, so we examine the chemistry expected in this system. In Figure 2 the electron energy distribution for three different electron temperatures is presented along with the collision cross section for the initial reactions by which electric power is coupled to the gas. There are several points to be made from this figure. First, the electron temperature must be very high compared to deposition temperatures, typically 800-1300 K, for a significant percentage of the electrons to dissociate or ionize the reactants. Even in a low temperature discharge, measured by the gas temperature, the electron energy must be high enough to produce ions to maintain the discharge. For hydrogen and methane, dissociation occurs at electron energies, 3 to 6 eV below where ionization sets in; higher cross sections are reached at the energies at which ionization sets in. Yet, to maintain the discharge, ionization must occur, so that some of the electrons have energies in the neighborhood of 14 to 18 eV.

Thus the initial reactive species concentrations are present at equivalent temperatures far above the gas temperature and certainly far above the substrate temperature. The initial system is far from equilibrium and any modeling of the process must start with this condition. The nonequilibrium condition is, of course, consistent with the fact that diamond is thermodynamically metastable with respect to graphite. The chemistry occurring between the super-equilibrium formation of active species and their striking the substrate surface is of interest. Thus models must start with the formation of active species and these may be different for the many techniques which have been used to produce diamond and diamond-like films.

The question of whether ions or free radicals play the dominant role in electrical discharge chemistry has not been resolved and must depend upon the specific system (see e.g., Avni and coworkers (17) or Marcus and Platzner (18)). Ion-molecule reaction rate coefficients are orders of magnitude greater than free radical rate coefficients but the ions are generated in smaller initial concentrations. Further, as ions recombine with electrons, also a very rapid process, they dissociate to produce hydrogen atoms or free radicals, e.g.,



Thus the nonequilibrium formation of ions plays a role in the production of super-equilibrium concentrations of hydrogen atoms and free radicals. H atoms are considered important in suppressing graphite buildup in competition with the deposition of diamonds (19), as well as in abstracting hydrogen atoms from the growing surface.

The observations that electric fields affect the rate of diamond deposition and the fact that plasmas contain ions, have led to proposals that ions are important in diamond deposition (11, 13, 20). All of these proposals incorporate positive ions, e.g., CH_3^+ in the mechanism. Tsuda et al. (20) describe a mechanism for diamond growth in which the diamond surface first becomes covered by methyl groups and then a methyl cation strikes the surface, simultaneously binding three methyl carbons to form the diamond structure. This concerted process does not allow the surface to graphitize. A very detailed mechanism is developed for which an activation energy of 27.4 kcal/mol is deduced. This is less than measured activation energies for diamond deposition which lie between 55 kcal/mol (19, 21) and 80 kcal/mol (19).

In the Frenklach-Spear mechanism (1) a hydrogen atom abstracts a hydrogen atom from a surface site where an acetylene molecule then adds. They develop a kinetic scheme from which an energy barrier of only 17.4 kcal/mol is obtained, even lower than for the Tsuda et al. mechanism and even further below the measured activation energy!

The implication of the importance of ions, because of the effect of electric fields, on the deposition of diamonds, coupled with the probably small concentration of ions relative to free radicals and other neutral species, suggests a mechanism in which an ion plays the role of a catalyst or the seed in a nucleation step, neutrals providing much of the ultimate mass.

The effectiveness of both positive and negative voltages clouds the picture. The source of positive ions is clear, but if negative ions, rather than electrons, are important, their source is not clear. Electron attachment may form a route for the formation of negative ions in hot wire or electrical discharge systems used to prepare diamond films. However, a calculation of the equilibrium constants from the free energies of formation as a function of temperature, shows that among the simple neutral species expected in the H_2/CH_4 system, the attachment of an electron to a hydrogen atom or CH radical is a candidate; equilibrium favors H^- below about 1800 K and CH^- below about 2200 K. The hydrogen reaction would require a third body. In the case of the hot filament, the negative ions could be formed on the filament. Catalytic decomposition or thermal decomposition could account for other species, including possibly, ions of both signs.

Negative ions have been observed (22, 23) in sooting flames but they have not been identified mass spectrometrically; they are assumed to be large molecular ions produced by electron attachment. In somewhat leaner, nonsooting flames, negative ions have also been identified, Figure 3, but their mechanism of formation is vague; they do not seem to be formed by simple attachment (24). They are present at about 1% of the positive ion concentration at an equivalence ratio of 1, stoichiometric flames, and their maximum concentration occurs at a higher equivalence ratio, fuel rich, than for positive ions. Their concentrations decrease with increasing total pressure. To my knowledge no measurements of the effect of voltage on diamond deposition in combustion systems have been made. Interestingly, diamonds are deposited from the flame in the region where soot is formed and where ions are present (25).

The growth species which adds to the ionic nuclei may be a stable molecule e.g., acetylene as suggested by Frenklach and Spear (1) or the methyl radical which has frequently been suggested (20). Angus (21) measured the rate of deposition of diamond in a hot filament environment to be first order in the methane pressure and one-half order with respect to ethylene pressure, from which he deduced that the growth mechanism must involve the addition of a species containing only one carbon atom. Similarly, Sato, Kamo, and Setaka (26) examined the effect of hydrocarbons, including alkanes, alkenes and acetylene on growth and Raman spectra of diamond films prepared in a microwave system and concluded that growth features and morphology are dependent approximately on the number of carbon atoms in the molecule. On the other hand, Fedoseev and associates (19) observed that the highest activation energy and the lowest rates were associated with growth from methane, and the lowest activation energy and the highest rates were associated with acetylene and that other hydrocarbons fell between these. This is reminiscent of the effect of molecular structure on both ion formation and soot formation in flames (2). Is there a connection?

CONCLUSIONS

The plasma condition seems to be a prerequisite for diamond film deposition, even by the hot filament technique and from a combustion flame. The ions in the plasma are at a concentration

considerably in excess of their equilibrium concentration at the substrate temperature, as are free radical and hydrogen atoms. Thus any model of the process must start with these conditions in the plasma. Both positive and negative ions (or electrons) seem to be involved. The source of positive ions is fairly clear, but the source and nature of negative ions are not. Because of the low concentration of ions compared to other species it is most likely that their role in diamond coating technology is analogous to that in flames, i.e., they act as nucleation agents, not as growth species.

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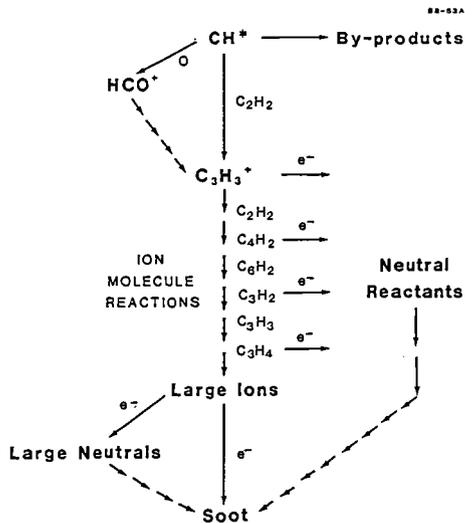


Figure 1. Ionic Mechanism for the Formation of Incipient Soot

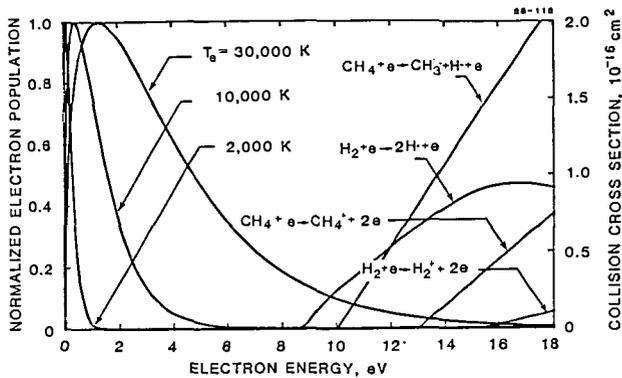


Figure 2. Electron Collision Dissociation of Methane and Hydrogen
 Ionization of Methane from Ref. 14.
 Dissociation of Methane from Ref. 15.
 Dissociation and Ionization of Hydrogen from Ref. 16.

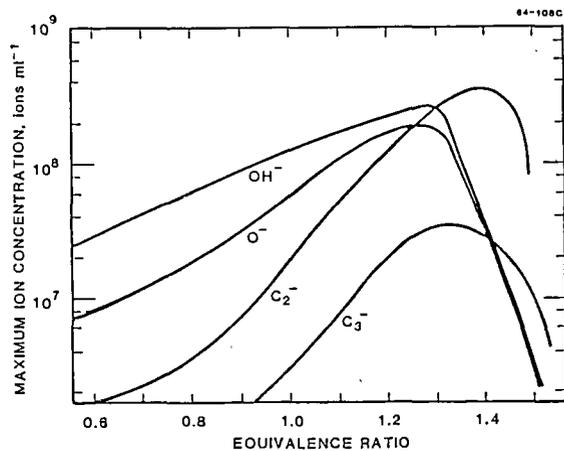


Figure 3. C_2H_2/O_2 Flame at 0.27 kPa.
 Total Fflow = $70 \text{ cm}^3/\text{s}$ (STP).