

## KINETICS OF METHANE PYROLYSIS IN HOT-FILAMENT REACTOR: EFFECT OF HYDROGEN

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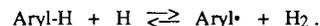
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### INTRODUCTION

A major breakthrough in low-pressure diamond deposition technology, that has led to micron-a-minute growth rates, began with the addition of molecular hydrogen to the reactive hydrocarbon mixtures [1-7]. Several factors have been suggested to explain the effect of the hydrogen dilution. First, and the most important one, is the preferential etching of graphite over diamond by hydrogen atoms [1,3,4,7-10]. This theory assumes that graphite and diamond are formed simultaneously but graphite (or, more generally, graphitic phase) is destroyed by reactions with H atoms whereas diamond is not, or at least not to the same extent. Deryagin and co-workers [1,3,4,8] argued that hydrogen atoms should be in a superequilibrium state for a successful growth of diamond. The requirement of the H superequilibrium (as opposite to just a high concentration of hydrogen atoms, which, for example, can be in partial equilibrium with H<sub>2</sub>) was rationalized by Frenklach and Spear [11] suggesting that a reversible H-atom abstraction reaction is the rate limiting step of the diamond surface growth. In a following work, using quantum mechanical methods, Huang *et al.* [12] computed that this reaction has a substantial energy barrier whereas subsequent steps of the diamond growth reaction sequence, acetylene addition to the surface radicals, have no energy barriers at all.

The second most frequently discussed [3,4,7] effect of hydrogen is to satisfy the dangling bonds of surface carbon atoms, thus keeping them in the *sp*<sup>3</sup> configuration and preventing the diamond surface from reconstruction into graphitic *sp*<sup>2</sup> (or carbynic *sp*) structures. Other possible roles of atomic hydrogen suggested are: to promote the production of acetylene, which was proposed to be the main monomer for diamond growth, in the gas phase [11]; to promote the *sp*<sup>3</sup> configuration of the gaseous radical precursors and surface clusters [13]; and to remove oxygen chemisorbed on the substrate [13].

The hydrogen effect was also attributed to the molecular hydrogen. Fedoseev *et al.* [3] suggested that "the addition of hydrogen to the initial hydrocarbon lowers its rate of decomposition, and therefore also the rate of formation of the solid phase." A recent computational study [14] examining the formation of polycyclic aromatic hydrocarbons (PAHs) in carbon-rich circumstellar envelopes revealed that the formation of aromatic structures, thought to be the precursors of carbonaceous solid phases [15-17], is entirely suppressed in the atmosphere of H<sub>2</sub> at high temperatures — temperatures that otherwise exhibit high growth rates of soot (and other forms of solid-phase carbon [18]) in fossil fuel air combustion [15] and argon-diluted pyrolysis [19]. The suppression phenomenon is explained [20-22] by the increase in the rate of the reverse direction of the abstraction reactions



It is predicted [14,22] that at lower temperatures this reaction is no longer rate-limiting and PAH growth is controlled by the rate of acetylene additions to aryl radicals. Under these conditions polycyclic aromatic hydrocarbons and solid carbon phases begin to appear.

There is an analogy between the conditions of PAH and carbon grain formation in circumstellar envelopes of carbon-rich stars [14,16,17] and CVD diamond deposition in hot-filament [23-25] and plasma-assisted [6,26] CVD reactors. In both processes the reaction takes place in hydrogen atmosphere; it is initiated by an intensive flux of energy, thermal or plasma; the reaction develops under the decrease in gas temperature; and the formation of the high molecular weight products, PAHs or diamond, occur at about the same temperatures, 800 – 1000 °C. The above theoretical considerations suggest that this analogy is not circumstantial. The results of the present computational study, aimed at the analysis of the effect of hydrogen on gaseous species under the conditions of diamond formation, demonstrate the similarity in gas-phase chemistry of the two processes, and suggest that the suppression of PAH production by molecular hydrogen plays the key role in diamond growth.

### COMPUTATIONAL MODEL

The model assumed for simulation of the gas-phase chemistry is a constant pressure, constant flow rate plug-flow reactor with an imposed temperature profile. This choice is based on the following considerations. First, diamond deposition characteristics obtained in experimental reactors of different geometries and energy sources are very similar [6] and, hence, it is more logical to begin modeling the process with a simplest case, hot-filament reactor, where gas activation can be assumed to be thermal. It will be argued elsewhere that the results obtained with this assumption are also applicable to plasma-assisted CVD reactors. Second, the idealization of the gas flow is a practical necessity as neither flow characteristics, which are required for development of the gas-dynamic model, nor species profiles, that can be used to test the model predictions, have been established experimentally. Finally, and most importantly, the objective of the present simulations is to study *qualitative* trends in the computed chemical species profiles, for which the numerical accuracy of the results is not critical.

The chemical reaction mechanism used here is based on the mechanism developed for the study of PAH production in carbon-rich circumstellar envelopes [14]. It is applicable to wide ranges of temperatures, 700 – 3000 K, and pressures, up to  $10^{-10}$  atm. The latter is compiled of 112 reactions and 39 species that describe, beginning with acetylene, the formation of benzene and its further growth to an infinitely large sized PAHs; this mechanism was adopted here without change. The 112 reactions of this mechanism were augmented with 19 reactions (adding 6 new species) describing the initial stages of methane pyrolysis: formation of  $\text{CH}_3$  and  $\text{CH}_2$  radicals and their subsequent reactions producing  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_3$ , the last two being the precursors of  $\text{C}_2\text{H}_2$ . The added reaction subset, along with the associated rate parameters, will be reported elsewhere.

The initial conditions for the "reference" case were assumed based on recent experiments of Harris *et al.* [25]: 0.3%  $\text{CH}_4$  –  $\text{H}_2$  mixture, pressure 20 torr, and the initial (inlet) reaction temperature 2600 K, which decreases linearly in time with the rate of 1400 K/s. Such a cooling rate means that the gas reaches the temperature of diamond deposition, ~ 1000 °C [26], within about 1 second. The computer simulations were carried until the temperature dropped to about 650 °C, well below the deposition conditions. The numerical integration of the differential equations describing the time-dependent species concentrations were performed with a constant-pressure kinetic code on a IBM 370–3090 computer at the Pennsylvania State University Computer Center using the LSODE integrator of Hindmarsh [27]. The relative error (parameter RTOL) was kept at  $1 \times 10^{-4}$  and the absolute error (parameter ATOL) was set well below the concentration of the principal PAH species.

### RESULTS AND DISCUSSION

The concentration profiles of major species computed for the "reference" case are similar to those obtained in constant-temperature computations of Harris *et al.* [25] and in plasma simulations of

Kline and co-workers [28]. These results indicate that  $C_2H_2$  is the major hydrocarbon species at the temperatures of diamond deposition. However, if the reaction time scale is decreased from 1 to  $1 \times 10^{-3}$  s (i.e., the temperature rate is changed from  $1.4 \times 10^3$  K/s to  $1.4 \times 10^6$  K/s),  $CH_4$  and  $CH_3$  become the predominant species. The residence times on the order of 1 ms have been reported by Yarbrough and Roy [23]. These authors modified the hot-filament reactor replacing the filament by bringing the gas to the substrate surface through a small-diameter tantalum tube which is heated by a surrounding wire coil to the hot-filament temperatures. Under such conditions the reaction mixture remains in contact with the hot tube for a relatively long period of time, on the order of milliseconds. As a result, the methane pyrolysis and hydrogen decomposition are accelerated by heterogeneous processes on the surface of the tube and the equilibrium between H and  $H_2$  is likely to establish before the gas leaves the tube. A gas-phase kinetic simulation with the "reference" case but assuming the initial concentration of hydrogen atoms to be  $[H]_{t=0} = ([H_2]/K_h)^{1/2}$ , where  $K_h$  is the equilibrium constant of reaction  $H + H = H_2$ , indicated that the concentration of  $C_2H_2$  reaches and supercedes that of  $CH_3$  at about 100  $\mu$ s. Thus, we conclude that under thermal activation of the gas phase acetylene should be the predominant hydrocarbon species at the conditions of diamond deposition, as initially suggested by Frenklach and Spear [11] and verified in recent optical [24] and mass-spectrometric [25] measurements.

To investigate the effect of hydrogen addition, a computer simulation was performed similar to the "reference" case but with argon instead of hydrogen as diluent. The numerical results obtained in these two cases are compared in Figs. 1 through 4. The H concentration is larger by about an order of magnitude in the  $H_2$  environment compared to that in the case of Ar (Fig. 1), which may support the H atom etching theory. The same information displayed in the form of H supersaturation, defined as

$$f = \frac{[H]}{[H]_{eq}} = \frac{[H]}{[H_2]/K_h},$$

shows that practically the same values of  $f$  are computed in the both cases. This result indicates that the H supersaturation itself is not a critical parameter. This is understandable since the  $f$  values are extremely large ( $\sim 10^7$  at 1000 °C), so that the kinetics of H atom reactions (e.g., etching) or of the following steps (e.g., acetylene addition) rather than their thermodynamics should be the controlling factors [22].

The concentration of  $CH_3$  is computed to be significantly larger in  $H_2$  than in Ar (Fig. 2), whereas the concentration of  $C_2H_2$  is practically the same in the both cases (Fig. 3). At first glance, these results may support the proposal of Tsuda *et al.* [29] that  $CH_3$  and not  $C_2H_2$  is the main "building block" for diamond film growth. Further computational tests, that will be discussed elsewhere, clarify this point. Now it is pertinent to note that since acetylene is the main reaction product of methane pyrolysis, the proximity in  $C_2H_2$  profiles computed in  $H_2$  and Ar environments (Fig. 3) demonstrates that the abundance of  $H_2$  does not lower the rate of methane decomposition. However, as seen in Fig. 4, the presence of  $H_2$  does pronouncedly suppresses the production of aromatic hydrocarbons. It is this suppression phenomenon that is proposed here to play the critical role in the hydrogen effect on diamond growth. Aromatic species formed in the gas phase condense on the (diamond) surface, i.e., collide with the surface and held there by van der Waals forces. Their further growth leads to the formation of graphitic layers, which competes with and thus prevents the growth of diamond.

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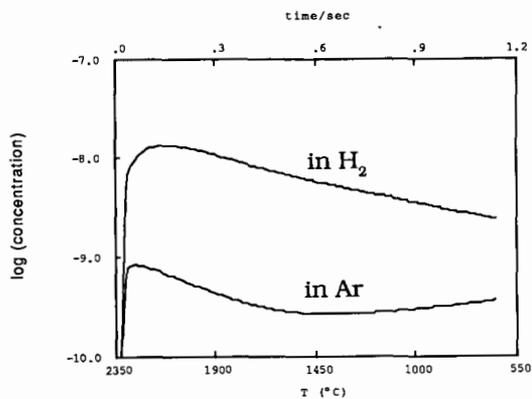


Fig. 1. Concentration of H

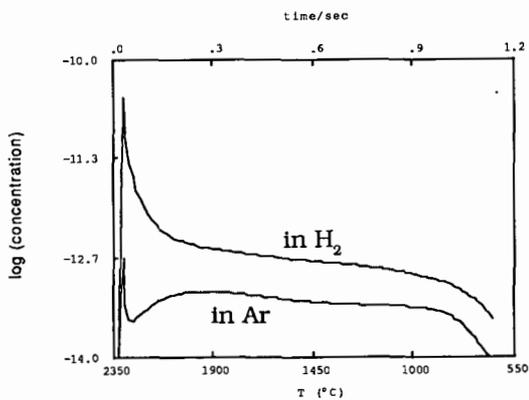


Fig. 2. Concentration of CH<sub>3</sub>

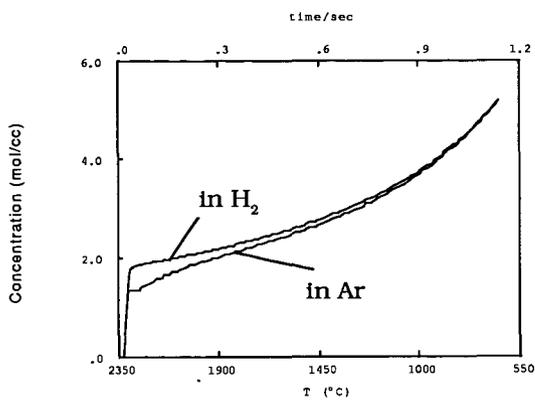


Fig. 3. Concentration of  $C_2H_2$

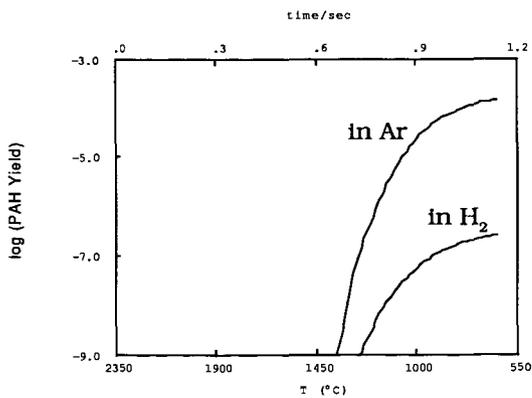


Fig. 4. Concentration of PAHs