Aromatic ring generation as a dust precursor in acetylene discharges

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Production of aromatic hydrocarbon compounds as an intermediate step for particle formation in low-pressure acetylene discharges is investigated via a kinetic approach. The detailed chemical reaction mechanism contains 140 reactions among 55 species. The cyclic hydrocarbon chemistry is mainly based on studies of polycyclic aromatic hydrocarbon formation in cosmic environments. The model explicitly includes organic chain, cyclic molecules, radicals, and ions up to a size of 12 carbon atoms. The calculated density profiles show that the aromatic formation yields are quite significant, suggesting that aromatic compounds play a role in the underlying mechanisms of particle formation in hydrocarbon plasmas. © 2006 American Institute of Physics.
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Reactive hydrocarbon plasmas are nowadays widely employed for the synthesis of carbon-based nanostructured films via the structural incorporation of plasma-grown nanoparticles, which act as building units for a myriad range of applications including electron field emitters.[1] However, in spite of the rising interest in nanoassembly processes in plasma technology, very little is known on the elementary chemical reactions underlying nanoparticle growth in hydrocarbon plasmas and especially the role of aromatic rings is still unclear. Knowledge of the mechanisms behind their origin is nevertheless indispensable if one wants to improve the control strategies for carbon nanoparticulate deposition.

Few experimental and theoretical studies on carbon clustering in low-pressure acetylene discharges exist and mainly focus on reactions between linear polyalkyne carbon chains.[2–5] On the other hand, the formation of carbon particles has extensively been investigated in astrophysical environments where polycyclic aromatic hydrocarbons (PAHs) are thought to be a dominant intermediate for the production of carbonaceous stellar dust that acts as a precursor for planet and carbon-rich circumstellar envelope formation.[6] PAHs have furthermore been suggested as a link towards the generation of soot particles during combustion in hydrocarbon flames.[7] A similar indication of the appearance of aromatic compounds seems to be present in low-pressure dusty acetylene discharges, where mass spectrometry and infrared absorption spectroscopy measurements show a change in the carbon cluster structure around six carbon atoms.[2,8] In this letter we investigate the assumption of possible involvement of cyclic rings in the first step of carbonaceous dust production by determining the number densities of the dominant aromatic precursors in acetylene-based discharges. The relative contribution of each aromatic species is calculated by the introduction of a detailed chemical kinetics mechanism in a one-dimensional (1D) fluid model, using acetylene as the precursor gas. A similar model has previously been applied to determine the potential building units of silicon nanocrystals in silane-based plasmas used for the fabrication of polymorphous hydrogenated silicon thin films (pm-Si:H) in solar cell applications.[9]

In this case, a one-dimensional parallel-plate discharge geometry is considered in a capacitively coupled radio frequency acetylene plasma, operated at a driving frequency of 13.56 MHz and a total gas pressure of 300 mTorr. Other discharge parameters include an electrode separation of 3 cm, a reactor radius of 32.5 cm, a uniform gas temperature of 400 K, and a total acetylene gas flow of 20 SCCM (SCCM denotes cubic centimeter per minute at STP). The flux and density profiles of each species (electrons, ions, radicals, aliphatic, and cyclic molecules) can be computed by solving the system of nonlinear particle balance equations on every of the 64 grid points considered in the axial discharge plane. The balance equations are in turn coupled to the Poisson equation for the calculation of the electric field, making the model fully self-consistent. A drift-diffusion approximation describes the transport of the different species towards the discharge walls, while a sticking module accounts for the plasma-wall interaction. Note that for the ion transport an effective electric field has been adopted, since the ions cannot follow the local instantaneous electric field due to inertial effects. The electron energy equation is also considered in order to obtain the average electron energy. A finite-difference technique is used for the numerical solution of the governing equations. Calculations are performed until successive iterations differ by no more than 0.0001%. More details on the numerical system and solution techniques can be found elsewhere.[9]

The complete set of chemical compounds and chemical reactions considered in the model consists of 55 species and approximately 140 reactions. Energetic electrons will first decompose the acetylene feed gas to small reactive radicals and ions, which can then trigger successive additive reactions involving C_2H_2 that ultimately lead to the formation of organic chain and cyclic molecules and higher polymerized cations and anions that contain up to a maximum of 12 carbon atoms. The growth of aliphatic molecules by C_2H_2 insertion and of aliphatic positive and negative ions by ion-molecule polymerization reactions has previously been

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TABLE I. Major chemical processes among the incorporated aliphatic molecules, radicals, and ions. More detailed information on these reactions can be found in Ref. 4.

	Reaction	Rate constant (cm^3 s^{-1})	
	Neutral-neutral reactions		
1.	$C_{2n}H + H_2 \rightarrow C_{2n}H_2 + H$	4.9×10^{-13}	$n = 1-6$
2.	$C_{2n}H + H \rightarrow C_{2n}H_2$	4.1×10^{-10}	$n = 1-6$
3.	$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H$	$\sim 5.8 \times 10^{-11}$	$n = 1-5$
4.	$H + C_{2n}H_2 \rightarrow C_{2n}H_3$	$\sim 5.0 \times 10^{-12}$	$n = 1-3$
5.	$C_{2n}H_2 + C_2H \rightarrow C_{2n+2}H_3$	2.2×10^{-12}	$n = 2-3$
6.	$H + C_{2n}H_3 \rightarrow H_2 + C_{2n}H_2$	6.6×10^{-11}	$n = 1-3$
7.	$C_2H + C_2H_2 \rightarrow C_{2n+2}H_2 + H$	6.6×10^{-11}	$n = 2-5$
8.	$C_2H_3 + C_nH \rightarrow C_2H_2 + C_nH_2$	$\sim 6.5 \times 10^{-11}$	$n = 1-2$
9.	$C_{2n}H_3 + H \rightarrow C_{2n-2}H_2 + C_2H_2$	$\sim 9.0 \times 10^{-11}$	$n = 2-3$
	Ion-neutral reactions		
10.	$C_{2n}H^- + C_2H_2 \rightarrow C_{2n+2}H^- + H_2$	1.0×10^{-12}	$n = 1-5$
11.	$H_2^+ + C_2H_2 \rightarrow C_2H_2^+ + H_2$	5.3×10^{-09}	
12.	$C_{2n}H_{2m}^+ + C_2H_2 \rightarrow C_{2n+2}H_{2m+2-2x}^+ + xH_2$	$\sim 1.2 \times 10^{-09}$	$n = 1-5;\ x = 0$ or 1
13.	$C_{2n}H^- + H_2^+ \rightarrow C_{2n}H + H + H$	$\sim 1.7 \times 10^{-07}$	$n = 1-6$
14.	$C_{2n}H^- + C_{2n}H_{2m}^+ \rightarrow C_{2n}H + C_{2n}H_{2m}$	$\sim 4.0 \times 10^{-08}$	$n = 1-6;\ m = 1-3$

investigated in Ref. 4 and forms the starting point of the present investigation. A condensed overview of all these relevant chemical processes is given in Table I. A further detailed discussion can be found in Ref. 4, where the role of the ions as possible precursors for carbonaceous dust formation has been evaluated. The emphasis of the present study is on the nominal amount of aromatic ring generation, and as such, we have developed here an additional chemical kinetic scheme that leads to cyclic ring generation.

So far we know of only one study reporting on aromatic chemistry in the low-pressure hydrocarbon plasma environment, in which a mechanism for soot formation in combustion of hydrocarbon fuels has been adopted.[5] However, some care has to be taken regarding the usage of rate coefficients from these kinds of mechanisms since many of the reaction rates have only been estimated for very high temperatures (~ 2000 K) and pressures (~ 1 atm) applicable to the pyrolysis conditions.[7] The scheme presented in this study is largely based on data from PAH formation in cosmic environments at much lower temperatures ($100-1000$ K) and pressures ($10^{-6}-10$ Torr), in which a shift of the dominant reaction pathways has been observed compared to the combustion theory.[6,10–12]

The incorporated hydrocarbon formation scheme is schematically illustrated in Fig. 1 and includes two major reaction steps: (i) the formation of the first aromatic ring from small aliphatics and (ii) the further growth towards additional rings. In this scheme the usual formalism for aromatic ring structures has been adopted, in which A_i denotes an aromatic ring molecule with i fused rings, while A_{i-} represents its radical containing an unpaired electron on the aromatic ring. Full arrows illustrate bimolecular and termolecular reactions involving acetylene, while atomic hydrogen reactions are represented by dashed arrows. For each chemical process the reaction rate coefficient is given in units of cm^3 s^{-1} and has been adopted from Refs. 6 and 10–12. The pathway explicitly considers the formation of the one- and two-ring compounds benzene (A_1) and naphthalene (A_2), their radicals A_{1-} and A_{2-}, and the phenylacetylene molecule (A_1C_2H) in which a hydrogen atom from the benzene ring has been substituted by an ethynyl group (C_2H). PAHs larger

than A_2 are lumped together as one species (i.e., PAH). Since little information exists on the subsequent growth of the second and larger aromatic rings, the mechanism is generally assumed to proceed through a set of three reactions: (i) addition of acetylene, (ii) hydrogen abstraction to form a radical, and (iii) a second addition of acetylene followed by ring closure. This repeated combination of H abstraction and C_2H_2 addition is better known as the HACA mechanism.

The primary emphasis here, however, is on the formation of the first aromatic ring compound benzene (A_1) and its radical (A_{1-}); by many perceived as the rate-limiting step in the reaction sequence towards larger aromatics.[6,7] Indeed, due to the delocalization of the electrons in the aromatic π cloud, rupture of the stable benzene ring structure seems highly unlikely. Hence, once the first ring is formed, consecutive reactions can only lead to the formation of substituted benzenes and larger PAHs by the HACA mechanism. This extra stability is also a factor that can point towards their production in dusty plasma environments. Several first-
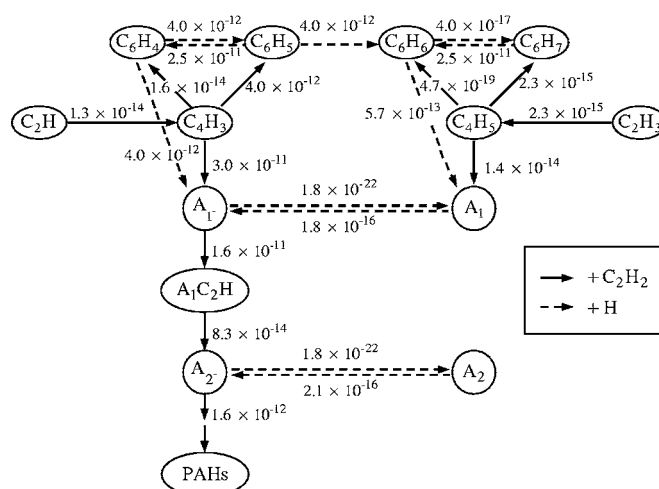

FIG. 1. Schematic representation of the major pathways towards aromatic hydrocarbon formation in low-pressure acetylene discharges. A key to the arrows is given at the right. The reaction rate coefficient of every chemical process is in units of cm^3 s^{-1}.
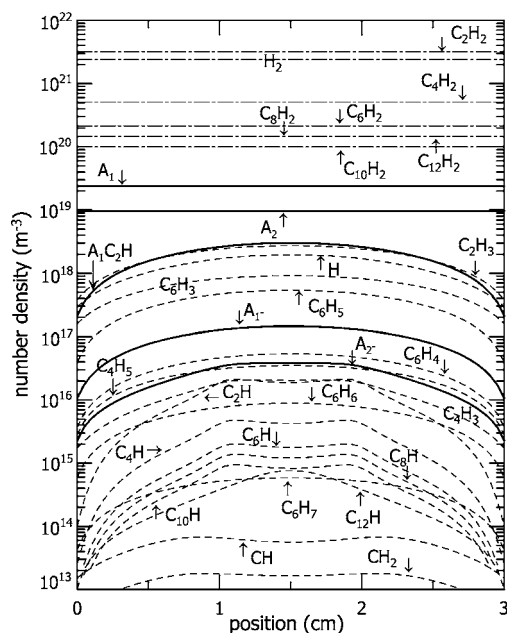
FIG. 2. Computed number densities of the dominant aliphatic parent molecules ($C_{2n}H_2$), free radicals, and aromatic compounds in a capacitively coupled radio-frequency acetylene discharge at $p=300$ mTorr, $\nu_{rf}=13.56$ MHz, and $T_{gas}=400$ K.

ring cyclization processes have been considered (see Fig. 1). The four-carbon-atom pathways involve the addition of acetylene to C_4H_3 and C_4H_5 which forms phenyl (A_1-) and benzene, respectively. Other possible routes to ring closure entail the cyclization of the C_6H_4 and C_6H_6 molecules. From the model we can deduce the most dominant reaction pathways for cyclic ring generation, and we find that around 73.5% is produced through the addition of acetylene to C_4H_3 and 25.7% via C_6H_4 cyclization. With 0.64% and 0.06% the C_6H_6 and C_4H_5 contributions are defined as negligible.

Figure 2 shows the calculated number density profiles of the most important aliphatic parent hydrocarbon molecules ($C_{2n}H_2$), free radicals, and aromatic compounds at roughly the first few seconds after discharge ignition when a final stationary state of the densities has been reached. All cyclic rings are represented by a solid line, while linear polyalkyne carbon chains and aliphatics that play a role in the aromatic ring generation and growth are displayed by a dashed line. Mainly species with even numbers of carbon atoms have been considered, since experimental observations have shown that the strong carbon bond structure of the initial acetylene molecule (H–C≡C–H) persists upon its succeeding integration in larger hydrocarbon species.[2] Species exhibiting a reactivity at the discharge walls can be identified by their decreasing density towards the electrodes. Nonradical molecules, on the other hand, are found to be homogeneously distributed throughout the entire reactor and are generally produced in larger amounts compared to their corresponding radicals. Besides the C_2H_2 feedstock gas, all other species are generated through chemical reactions in the ionized gas phase.

One of the interesting observations is that at 400 K the amount of produced aromatic compounds is quite significant. While most reactive linear and cyclic precursors of the aromatic ring growth exhibit a density which is somewhat higher or comparable to the concentration of the other important radicals considered in the discharge, the stable benzene and naphthalene molecules are present at the relatively high amounts of 2.4×10^{19} and 9.6×10^{18} m^{-3}, respectively. Note that the acetylene feed gas density is only about two orders of magnitude higher (at 3.2×10^{21} m^{-3}). This result confirms the experimental findings that aromatic rings are present in low-pressure hydrocarbon plasmas and can grow further towards larger PAHs.

In summary, we have shown that aromatic compounds can grow from smaller aliphatic species in low-pressure capacitively coupled acetylene discharges at conditions relevant to particle formation. In contrast to the mechanisms explaining soot production in flames, the aromatic chemistry presented here is based on PAH formation in cosmic environments, in which chemical data are provided for gas temperatures and pressures also applicable to low-pressure plasma systems. In the present one-dimensional fluid model the most important pathway towards the closure of the first aromatic ring is the addition of acetylene to C_4H_3, which accounts for 74% of the total phenyl (c-C_6H_5 or A_1-) production. From the computed number density profiles of the aliphatic and aromatic species a substantial amount of aromatic ring generation can be deduced. Similar to chemical models for dust production in cosmic environments, we therefore suggest that polycyclic aromatic compounds play an important role in the formation of carbonaceous nanoparticles.

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