The Chemistry of Cosmic Dust Analogs from C, C₂, and C₂H₂ in C-rich Circumstellar Envelopes

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Abstract

Interstellar carbonaceous dust is mainly formed in the innermost regions of circumstellar envelopes around carbon-rich asymptotic giant branch stars (AGBs). In these highly chemically stratified regions, atomic and diatomic carbon, along with acetylene, are the most abundant species after H₂ and CO. In a previous study, we addressed the chemistry of carbon (C and C₂) with H₂ showing that acetylene and aliphatic species form efficiently in the dust formation region of carbon-rich AGBs whereas aromatics do not. Still, acetylene is known to be a key ingredient in the formation of linear polycyclic chains, benzene, and polycyclic aromatic hydrocarbons (PAHs), as shown by previous experiments. However, these experiments have not considered the chemistry of carbon (C and C₂) with C₂H₂. In this work, by employing a sufficient amount of acetylene, we investigate its gas-phase interaction with atomic and diatomic carbon. We show that the chemistry involved produces linear polycyclic chains, benzene, and other PAHs, which are observed with high abundances in the early evolutionary phase of planetary nebula. More importantly, we have found a nonnegligible amount of pure and hydrogenated carbon clusters as well as aromatics with aliphatic substitutions, both being a direct consequence of the addition of atomic carbon. The incorporation of alkyl substituents into aromatics can be rationalized by a mechanism involving hydrogen abstraction followed by methyl addition. All the species detected in the gas phase are incorporated into nanometric-sized dust analogs, which consist of a complex mixture of sp, sp², and sp³ hydrocarbons with amorphous morphology.

Unified Astronomy Thesaurus concepts: Asymptotic giant branch (108); Post-asymptotic giant branch (1287); Circumstellar matter (241); Circumstellar dust (236); Laboratory astrophysics (2004); Molecular physics (2058); Plasma physics (2089); Protoplanetary nebulae (1301)

1. Introduction

Carbonaceous dust is ubiquitously found in space, from the interstellar medium (ISM) to nova ejecta and circumstellar shells (Chiar et al. 2013). Astronomical observations in the mid-infrared (MIR) range reveal the presence of both aromatic and aliphatic dust components. In the diffuse ISM, the 3.4 μm absorption band (assigned to the CH vibrational stretching modes of CH₂ and CH₃ aliphatic moieties), along with the weaker absorption features at 6.8 and 7.3 μm (which correspond to the CH bending modes of aliphatic groups), have been attributed to hydrogenated amorphous carbon (Pendleton & Allamandola 2002; Dartois et al. 2004). On the other hand, the so-called aromatic infrared emission bands (AIBs) are widely observed in environments of our Galaxy that are submitted to ultraviolet (UV) photons (Peeters et al. 2002, 2004). The AIBs, which fall in the spectral range from 3 to 20 μm (main bands at 3.3, 6.2, 7.7, 8.6 and 11.2 μm) have generally been assigned to polycyclic aromatic carriers that are small enough to be stochastically heated by the absorption of a single UV photon, which constitutes the polycyclic aromatic hydrocarbon (PAH) hypothesis (Leger & Puget 1984; Allamandola et al. 1985, 1989; Puget & Leger 1989). There is also observational evidence for an evolutionary scenario from aliphatics to aromatics calling for very small grains of mixed aliphatic–aromatic composition both in evolved star environments (Goto et al. 2003; Kwok & Zhang 2011) and in molecular clouds (Pilleri et al. 2015). Overall, these observations call for a better understanding of the formation of PAHs and of carbon dust in general in astrophysical environments.

In our Galaxy, carbon-rich (C-rich) asymptotic giant branch (AGB) stars are the major sources of carbonaceous dust (Gehrz 1989), thus chemical models have been developed to account for the formation of PAHs and hydrogenated carbon clusters in these environments (e.g., Pascoli & Polleux 2000; Cherchneff 2011). According to observations, acetylene (C₂H₂) is one of the most abundant molecules in the inner regions of circumstellar envelopes (CSEs) where dust is formed, presenting a relative abundance to H₂ of 8 × 10⁻³ (Fonfría et al. 2008), while carbon atoms are also expected to be highly abundant. Chemical equilibrium calculations predict the concentration of carbon atoms to be 1–2 orders of magnitude below that of C₂H₂ in the region where carbon molecules are expected to condense into dust (Agúndez et al. 2020).
It is well known that the polymerization of C\textsubscript{2}H\textsubscript{2} gives rise to polyacetylenic chains (Cernicharo 2004), whose formation mechanism has been recently mapped with the Atacama Large Millimeter/submillimeter Array in the outer regions of the C-star envelope IRC +10216 (Agúndez et al. 2017). Furthermore, diacetylene (C\textsubscript{4}H\textsubscript{2}) has been recently detected in this star through high spectral resolution MIR observations (Fonfría et al. 2018). Acetylene is also believed to play a crucial role in the formation of benzene and PAH compounds (Frenklach & Feigelson 1989). The formation of benzene in evolved stars has been rationalized from experiments of C\textsubscript{2}H\textsubscript{2} pyrolysis by the reaction of two propargyl (C\textsubscript{3}H\textsubscript{3}) radicals (Miller & Melius 1992), a mechanism that requires high temperatures and high acetylene concentrations, which are not encountered in the dust nucleation zone of AGB stars. The temperature in the region between two and four stellar radii is estimated to be in the range from 1500 to 1000 K whereas a density of acetylene of \(10^7\) molecules cm\(^{-3}\) has been derived by Fonfría et al. (2008). This abundance for acetylene is in very good agreement with recent model predictions for C-rich AGB stars (Agúndez et al. 2020).

Another chemical route for the formation of benzene, considering neutral–neutral reactions, and at much lower temperatures than those needed in combustion theory, has been derived from acetylene discharges. It proceeds mainly by the addition of C\textsubscript{2}H\textsubscript{2} to the C\textsubscript{4}H\textsubscript{2} radical and to a lesser extent by the cyclization of C\textsubscript{6}H\textsubscript{4} (De Bleecker et al. 2006a). Further growth from benzene to PAHs is assumed to take place through the so-called hydrogen abstraction acetylene addition (HACA) mechanism (Frenklach & Warnatz 1987; Frenklach & Feigelson 1989; Shukla & Koshi 2012; Yang et al. 2016). Recently, a chemical route for the growth of large benzoid-PAHs (comprised only of six-membered ring structures) has been proposed through the so-called hydrogen abstraction vinylacetylene addition (HAVA) mechanism (Zhao et al. 2018). Thus, complementary HACA/HAVA mechanisms might be needed for the molecular growth of PAHs in circumstellar environments.

Several laboratory experiments have dealt with the formation of stardust analogs from acetylene, either in dusty plasmas (Kovačević et al. 2005; Stefanović et al. 2005), in pyrolysis experiments (Binnier et al. 2009; Jäger et al. 2009) or in molecular jets exposed to plasma discharges (Contreras & Salama 2013). However, all of them lack the addition of atomic carbon and therefore are not suitable for evaluating its impact on the growth of hydrocarbons with implications on, e.g., the formation of hydrocarbons with an odd number of carbon atoms (Cernicharo 2004).

Recently, we have shown that sputtering gas aggregation sources (SGASs) are particularly suited for studying dust formation in the CSE of AGBs (Martínez et al. 2020). In particular, we have demonstrated that the interaction of atomic carbon with molecular hydrogen promotes the formation of nonaromatic molecules, acetylene being one of the main gas-phase products. Here, we expand our previous work to investigate the interaction of atomic carbon with acetylene due to its known importance in the formation and growth of hydrocarbons. In order to accelerate the chemistry between carbon and acetylene so as to have access to most of the reaction pathways, as well as to investigate different conditions which would pertain to different regions of the CSE, we have intentionally increased the concentration of acetylene. In addition, our experimental conditions are also of interest for studying the envelopes of C-rich protoplanetary nebulae (PPNe) in which the UV radiation from the central star provokes the photodissociation of acetylene and methane, providing a high abundance of carbon initiating a rich chemistry involving C, C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{4} and other hydrocarbons (Cernicharo 2004).

We have found that, unlike what is commonly observed for dust analogs prepared in pyrolysis experiments or plasmas, a nonnegligible amount of the produced material consists of carbon clusters (both pure and hydrogenated) with an odd number of carbon atoms, being a direct consequence of the interaction of atomic carbon with acetylene. Additionally, aromatics with aliphatic substitutions have been observed. We suggest that the formation of alkyl-substituted aromatics proceeds through the formation of CH\textsubscript{3} radicals, which is also a consequence of the addition of atomic carbon.

2. Experiments

For the production and analysis of the dust analogs we employed the Stardust machine. The technical details of Stardust can be found elsewhere (Martínez et al. 2018, 2020). The particular experimental setup used in this work is schematically depicted in Figure 1. A pictorial view of the CSE region simulated by our experimental setup can be found in Martínez et al. (2020). The base pressure of the system is in the 10\(^{-10}\) mbar range and the pressure during the production of the analogs at different positions of the machine is also indicated in Figure 1.

Dust analogs were produced with a scaled-up multiple ion cluster source (MICS) (Martínez et al. 2012), a special type of SGAS, working in ultrahigh vacuum (UHV) conditions (Haberland et al. 1991). Atomic carbon was delivered by magnetron sputtering of a 2 inch graphite target (99.95% purity) using Ar as sputtering gas with a flow rate of 150 sccm.
The sputtered atoms coalesce inside the aggregation zone (aggregation length, i.e., distance from the magnetron target to the exit nozzle: 374 mm). Acetylene (purity ≥ 99.6%, diluted in acetone) was injected in the aggregation zone of the MICS through a lateral entrance at constant flow rates of 0, 4 × 10⁻⁴, 0.15, and 1 sccm. The DC magnetron was regulated in current and 0.2 A (corresponding to 100 W) were applied.

Optical emission spectroscopy (OES) was performed inside the aggregation zone (at OES position in Figure 1) and the light emitted by the sputtering plasma at a distance of around 1 cm from the magnetron target was collected through a fused silica window and a fused silica optical fiber. A 193 mm focal length, motorized Czerny–Turner spectrometer (Andor, model Shamrock SR-193-i-A) equipped with a CCD camera (iDus DU420A-BVF) was employed. Two diffraction gratings with 1200 and 1800 grooves mm⁻¹, installed in a movable turret, provide spectral ranges of 300–1200 nm and 200–950 nm, respectively, and nominal spectral resolutions of 0.22 nm and 0.15 nm, respectively (for an input slit width of 20 μm). The relative spectral efficiencies of the spectroscopic equipment were quantified for both diffraction gratings with a calibrated tungsten lamp.

Mass spectrometry was used for in situ analysis of the gaseous species produced during the production of the dust analogs. This was performed at positions labeled as QMS1 and QMS2 in Figure 1. At QMS1 a quadrupole mass spectrometer (PrismaPlus, Pfeiffer) with a mass range of 0–100 amu and a Faraday cup detector was used. At QMS2, a Pfeiffer HiQuad QMG 700 with QMA 400 mass spectrometer (mass range of 0–512 amu) equipped with a CP 400 ion counter preamplifier was used, which enabled a higher sensitivity. The pressure in the UHV chamber at position QMS1 during the analog production precludes the use of a more sensitive secondary electron multiplier detector. Specific chemical compounds have been tentatively assigned from mass spectra considering the fragmentation pattern by electron impact ionization available at the NIST database (NIST Mass Spectrometry Data Center et al. 2020).

Morphological characterization of the analogs was performed ex situ by atomic force microscopy (AFM) and transmission electron microscopy (TEM). In both cases the deposits were collected through sample entry 1 of Figure 1. For the AFM measurements the dust analogs were collected on SiO₂ substrates whereas carbon grids were employed for TEM. The AFM measurements were carried out with a Cervantes AFM System equipped with Dulcinea electronics from Nanotec Electronica S.L. All images were recorded and analyzed using the WSXM software (Horcas et al. 2007). TEM was performed with a FEI-TITAN X-EG transmission electron microscope used in scanning mode and operated at 300 kV and at 120 kV. The images were acquired using a high-angle annular dark field detector. The microscope was equipped with a monochromator, Gatan Energy Filter Tridiem 866 ERS, a spherical aberration corrector for the electron probe (which allows for an effective spatial resolution of 0.08 nm), and an energy dispersive X-ray detector for energy dispersive spectroscopy analysis.

The composition of the dust analogs was investigated in situ by infrared spectroscopy in transmission geometry. The dust analogs were deposited on KBr substrates and transferred to a separated UHV chamber by means of a UHV suitcase (P < 5 × 10⁻⁹ mbar). This protocol ensured that the inspected deposits were not air-contaminated. A VERTEX 70 V (Bruker) instrument was employed and the complete optical path was kept in vacuum. The spectral resolution was set to 2 cm⁻¹ and 256 scans were coadded. A liquid nitrogen-cooled mercury cadmium telluride detector was used. For the analysis of the IR spectra, spectral deconvolution was performed when peaks were not resolved due to overlapping of IR bands.

Finally, the molecular composition of the analogs was investigated ex situ by laser desorption/ionization mass spectrometry (LDI-MS) employing the Aromatic Research of Organics with Molecular Analyzer (AROMA) setup (Sababou et al. 2017) using the so-called laser desorption—laser ionization scheme in which desorption and ionization are separated in time and space and performed with two different lasers. The desorption step was performed with the fundamental mode of a Nd:YAG laser (λ = 1064 nm) whereas the ionization step was performed employing the fourth harmonic of a Nd:YAG laser (λ = 266 nm). This scheme is particularly sensitive to PAHs due to the wavelength of the ionization laser. The ions generated are stored and thermalized in a linear quadrupole ion trap and subsequently monitored by time-of-flight mass spectrometry.

3. Results

3.1. Gas-phase Molecules Produced during Formation of the Dust Analogs

Figure 2(a) shows the optical emission spectra during the dust analog formation inside the aggregation zone of the MICS in the spectral regions corresponding to the CH (A–X) band, the
C₂ Swan band ($d^3\Pi^g - a^3\Pi^g$), and the $H_\alpha$ line of the Balmer series for the different C₂H₂ flow rates employed. When no C₂H₂ was injected inside the aggregation zone, the molecular C₂ Swan band is clearly observed. Since the sputtering of graphite in the SGAS produces mainly atomic carbon, we rationalize that C₂ is formed via the three-body reaction C + C + Ar $\rightarrow$ C₂ + Ar (Martínez et al. 2020), which involves Ar atoms from the sputtering gas used.

As C₂H₂ is injected, the C₂ Swan band vanishes and a clear signature of the presence of atomic hydrogen is observed through the appearance of the $H_\alpha$ line. This suggests that the excited C₂ is consumed to some extent in the reaction C₂ + C₂H₂ $\rightarrow$ C₃H + H, which is known to be rapid even at low temperatures (Canosa et al. 2007; Daugey et al. 2008). In addition, as C₂H₂ is injected, it can directly react with atomic carbon through, e.g., C + C₂H₂ $\rightarrow$ C₃H + H and/or C + C₂H₂ $\rightarrow$ C₃ + H₂ (Clary et al. 2002), which diminishes the amount of atomic carbon available to form C₂ and releases atomic hydrogen as well. Furthermore, emission from the CH radical is detected for the two highest flow rates investigated.

We have already shown that this radical can be formed by the interaction of atomic carbon with H₂ at very low densities, even with the residual H₂ in the UHV chamber (Martínez et al. 2020). The concurrent detection of the H₂ line suggests an excess of atomic hydrogen which, if it is not participating in further chemical reactions, will recombine into H₂ by three-body reactions, thus increasing the overall H₂ density. The bimolecular reaction C + H₂ $\rightarrow$ CH + H is highly endothermic unless atomic carbon is electronically excited (Sato et al. 1998). The reaction of C with vibrationally excited H₂ could help in overcoming the barrier energy but under the physical conditions of the Stardust machine we do not expect high abundance of H₂ in the v = 1, 2 vibrational levels. Therefore, CH is most probably formed by a three-body reaction involving Ar (sputtering gas) as third body (C + H + Ar $\rightarrow$ CH + Ar), although we cannot completely rule out a contribution from the dissociation of C₂H₂ in the magnetron plasma. From gas flow calculations, we have estimated that around 2% of the injected C₂H₂ reaches the magnetron and is therefore susceptible to dissociate by electron impact.

In order to investigate the molecular species that are formed during dust analog production, we have performed in situ mass spectrometry at position QMS1 in Figure 1. Once at this position, no further growth of the analogs takes place. Therefore, growth in the production of the analogs is carried out in the absence of C₂H₂, only Ar, which is used as sputtering gas, and the residual gases in the chamber (H₂, H₂O and CO) are detected (Figure 3(a)). The peak at m/z = 80 corresponds to the formation of Ar dimers (Ar₂) during the gas expansion through the nozzle of the MICS.

In contrast, when C₂H₂ is injected we detect diacetylene (C₆H₄) and for the highest flow rates employed also triacetylene (C₆H₆) (Figure 3(a)). The polymerization of C₂H₂ to larger linear polyacetylenic chains is known to occur through the reaction with the ethynil radical (C₂H) via C₂H + C₂nH₂ $\rightarrow$ Cₙ₊₁H + H. More interestingly, for the highest C₂H₂ flow rate we have clearly detected C₆H₄ and C₆H₆ (Figure 3(c)). C₆H₄ has been suggested to be involved in the formation of benzene through a cyclization mechanism (De Bleecker et al. 2006a) and the concomitant detection of both species in our experiments seems to support this mechanism.

As shown in Figure 3(d), the formation of all the molecules detected by mass spectrometry is accompanied by the consumption of C₂H₂ once atomic carbon is released from the magnetron target. In addition, we have observed the production of H₂ (m/z = 2). Atomic hydrogen is produced in high amounts by the polymerization reactions of C₂H₂, thus it is available to participate in further chemical reactions, including its recombination to molecular hydrogen by three-body reactions.
The signals corresponding to H$_2$O ($m/z = 18$) and CO$_2$ ($m/z = 44$) were stable, indicating that they were not involved in the chemical reactions. However, we observed slight changes in the signal associated with the main fragment of acetone ($m/z = 43$), which is present as an impurity in the C$_2$H$_2$ (concentration lower than 0.3%), along with a slight increase in the amount of CO ($m/z = 28$). Nevertheless, we did not detect any other gas-phase O-bearing molecule, implying that the acetone impurity in C$_2$H$_2$ is only weakly (if any) contributing to the chemistry involved in the formation of the analogs. Moreover, the reaction between C and H$_2$O has a very large barrier of $\sim$20,000 K (Mayer et al. 1967) and that of C with CO$_2$ has been measured at 300 K with a rate below $10^{-15}$ (Husain & Young 1975); thus, the formation of O-bearing species is very unlikely in our experiments.

Higher-sensitivity gas-phase mass spectrometry was performed at position QMS2 in Figure 1 for the highest C$_2$H$_2$ flow rate (Figure 3(e)). The differences observed in the relative intensities among C$_5$H$_6$, C$_6$H$_6$, C$_7$H$_6$, and Ar$_2$ in Figures 3(c) and (e) are due to the different sensitivity of the QMS as well as the different pressures at locations QMS1 and QMS2. Concerning polyacetylenic chains, we detected up to C$_5$H$_2$. Furthermore, apart from C$_6$H$_6$, we observed the formation of larger aromatic molecules including naphthalene (C$_{10}$H$_8$), acenaphthylene (C$_{12}$H$_8$), and biphenyl/ethynylphthalalene (C$_{12}$H$_{10}$). These molecules are important for the growth of larger PAHs through different mechanisms including the well-known HACA mechanism (Shukla & Koshi 2012). We have also detected phenylacetylene (C$_6$H$_5$) which is a stable intermediate in the growth of naphthalene from benzene through the HACA mechanism. Interestingly, unlike what is observed in acetylene pyrolysis (Shukla & Koshi 2012) or acetylene discharges (Deschenaux et al. 1999), we have detected aromatic molecules with aliphatic substitutions (toluene (C$_7$H$_8$), styrene (C$_8$H$_8$), and xylene/ethylbenzene (C$_8$H$_{10}$)). The HACA mechanism does not explain the formation of aromatic compounds with aliphatic substituents. However, the addition of C and its interaction with H$_2$ (both residual in the UHV system and formed by recombination of the released atomic hydrogen) promotes the formation of alkyl radicals, which open up chemical routes for the formation of alkyl-substituted aromatics (see Section 4).

Finally, we detected a number of hydrogenated carbon clusters (HC-clusters) of aliphatic nature with odd numbers of carbon atoms from C$_5$ to C$_{11}$, again differing from what is found in acetylene discharges/pyrolysis in which predominantly molecules with even numbers of carbon atoms are formed (see Figure 3(e)). The apparent absence of C$_7$ HC-clusters might be due to a blurring of the signal by the peaks associated with toluene and its main fragment ($m/z = 91/92$). For C$_3$ clusters, it is the Ar signal that precludes its detection. The production of these C-clusters is a clear signature of the interaction of atomic carbon with C$_2$H$_2$. The reaction of C and C$_2$H$_2$ is known to be fast, yielding C$_3$ and/or C$_3$H (Liao & Herbst 1995; Clary et al. 2002). Analogous reactions of C with larger polyacetylenic chains are also an efficient way to produce hydrocarbons with odd numbers of carbon atoms in chemical environments where C and C$_2$H$_2$ are abundant (Cernicharo 2004). In addition, the reaction of C with other large hydrocarbons is known to occur very rapidly and without a barrier (Haider & Husain 1992; Liao & Herbst 1995; Husain & Ioannou 1997).

Overall, the results concerning in situ mass spectrometry evidence the formation of three different families of gas-phase chemical compounds, namely polyacetylenic chains, aromatic species, either pure or with aliphatic substitutions, as well as C- and HC-clusters of aliphatic nature. The identified masses are listed in Table 1 along with their tentative assignments to chemical compounds (NIST Mass Spectrometry Data Center et al. 2020). A detailed description of the possible formation mechanisms is provided in Section 4.

### Table 1

| $m/z$ | Chemical formula | Compound |
|------|------------------|----------|
| 26   | C$_3$H$_2$        | acetylene |
| 50   | C$_4$H$_2$        | diacetylene |
| 74   | C$_6$H$_2$        | triacetylene |
| 98   | C$_8$H$_2$        | octatetraene |

**Aromatics**

| $m/z$ | Chemical formula | Compound |
|------|------------------|----------|
| 78   | C$_8$H$_6$        | benzene |
| 91/92| C$_{10}$H$_6$     | toluene |
| 102  | C$_{12}$H$_6$     | phenylacetylene |
| 104  | C$_{12}$H$_8$     | styrene |
| 106  | C$_{10}$H$_8$     | xylene/ethylbenzene |
| 128  | C$_{14}$H$_8$     | naphthalene |
| 152  | C$_{16}$H$_8$     | acenaphthylene |
| 153/154 | C$_{13}$H$_{10}$ | biphenyl/ethynylphthalalene |

**Aliphatics**

| $m/z$ | Chemical formula | Compound |
|------|------------------|----------|
| 62–68| C$_{5}$H$_{10}$   | C$_5$-clusters |
| 76   | C$_{6}$H$_{11}$   | 3-hexene-1,5-diyne |
| 115–123 | C$_{6}$H$_{12}$   | C$_6$-clusters |
| 140–144 | C$_{7}$H$_{12}$   | C$_7$-clusters |

**Figure 4.** Morphology of the dust analogs without (top) and with (bottom) C$_2$H$_2$ injection (flow rate of 1 sccm). (a, b) Atomic force microscopy (AFM) images. (c, d) Size distribution extracted from AFM images. The blue lines correspond to the fitting to log-normal distributions. (e, f) Transmission electron microscopy images.

#### 3.2. Morphology of the Dust Analogs

Apart from the gas-phase species, most of the material produced during the formation of the dust analogs consists of particles with diameters in the nanometer range (Figure 4). Due to the low kinetic energy of the particles produced using gas.
aggregation sources, the particles soft-land on the substrate and thus retain the gas-phase morphology and structure.

Figures 4(a) and (b) show typical AFM images of the dust analogs when no C$_2$H$_2$ was injected in the aggregation zone (pure C particles) and for a C$_2$H$_2$ flow rate of 1 sccm, respectively. In both cases nanoparticles (NPs) are observed with mean NP diameters of 9.3 and 7.0 nm for pure C NPs and for a C$_2$H$_2$ flow rate of 1 sccm, respectively. However, a broader size distribution is obtained when injecting C$_2$H$_2$ (see Figures 4(c) and (d)). Moreover, the production rate increased enormously when C$_2$H$_2$ was injected (by a factor around of 350 in terms of collected NPs/μm$^2$s), which evidences the interaction of atomic C with C$_2$H$_2$, resulting in a manifest acceleration of the chemistry.

The TEM analysis of the NPs revealed the formation of amorphous NPs irrespective of the injection of C$_2$H$_2$ (Figures 4(e)–(f)). The main difference consists in the shape of the particles. Pure C NPs present a well-defined round shape whereas those formed after C$_2$H$_2$ injection tend to agglomerate. This agglomeration is observed in the AFM images as well, but it is more clearly seen in the TEM images. Diffusion of the NPs once deposited on the substrates is not expected, thus the agglomerates might be already formed in the gas phase.

![Figure 5. (a) IR spectrum of the dust analog. (b) Spectral deconvolution in the range 1500–1750 cm$^{-1}$. For the deconvolution, a baseline has been subtracted to remove the contribution from the very broad amorphous carbon band.](image-url)
corresponds to the $-\text{C} \equiv \text{C} -$ stretching mode of monosubstituted acetylene. In addition, a second $-\text{C} \equiv \text{C} -$ stretching mode is observed at 2200 cm$^{-1}$ which is ascribed to the stretching mode of conjugated triple bonds $-\text{C} \equiv \text{C} - \text{C} \equiv \text{C} -$ (Socrates 2001). This band is also found in dust from acetylene plasmas (Stoykov et al. 2001) but is often too weak to be observed (Kovačević et al. 2005; Stefanović et al. 2005). In addition, it is not commonly observed in dust analogs from acetylene pyrolysis (Biennier et al. 2009). The fact that we observe this band might be related to the addition of atomic carbon and the formation of C$_2$, which in the end increases the formation of linear polyacetylenic chains via the C$_2$H radical route (see Section 4).

On the other hand, numerous bands indicate the presence of sp$^3$ carbon and aliphatic moieties. The bands at 1369 cm$^{-1}$, 1379 cm$^{-1}$, and 1445 cm$^{-1}$, assigned to the CH$_3$ symmetric bending and CH$_3$ asymmetric bending/CH$_2$ scissoring modes, respectively (see Table 2), are a clear signature of alkyl moieties. These bands are accompanied by those in the region between 3000 and 2800 cm$^{-1}$, which correspond to the CH$_2$ and CH$_3$ stretching modes. Moreover, the band at 968 cm$^{-1}$ is ascribed to the CH$_3$ rocking mode.

Concerning sp$^2$ carbon, the bands at 1600, 1578, 1492, and 1437 cm$^{-1}$ reveal the presence of aromatics in the dust analogs. All are assigned to aromatic C = C stretching modes. In the case of alkyl substituted aromatics, the band at 1578 cm$^{-1}$ is usually a shoulder of that at 1600 cm$^{-1}$, as in our case. Moreover, the band at 1492 cm$^{-1}$ is intense for substituted aromatics (Socrates 2001). These results are consistent with the detection of aromatics with aliphatic substituents by mass spectrometry and reveal that the aromatic compounds incorporated into the dust analogs are not only pure but contain aliphatic substituents as well. We note that a similar result has been recently obtained by Gaiván et al. (2020) during the formation of dust analogs using small PAHs as precursors in a molecular jet exposed to an electrical discharge.

Other bands related to the aromatic compounds incorporated into the dust analogs are the CH out-of-plane bending modes. The different bands observed at 890 cm$^{-1}$, 843 cm$^{-1}$, 776 cm$^{-1}$, and 756 cm$^{-1}$ are related to different numbers of peripheral adjacent H atoms (solo, duo, trio, and quartet, respectively) (Hony et al. 2001; Carpentier et al. 2012) and are characteristic of PAHs, although insensitive to PAH substitution. However, the band at 700 cm$^{-1}$ can be assigned to the CH out-of-plane bending mode of substituted benzenes (Socrates 2001). Finally, the band at 640 cm$^{-1}$ is attributed to the CCC in-plane bending of aromatic compounds (Gadallah et al. 2012) and the combination band at 1938 cm$^{-1}$ is ascribed to the combination of out-of-plane and in-plane CH bending modes (combination and overtone bands in the spectral region 2000–1700 cm$^{-1}$ are characteristic of aromatic compounds).

Apart from aromatic compounds, there are also bands related to olefinic sp$^2$ carbon. The sp$^2$ CH stretching bands in the region 3100–3000 cm$^{-1}$ are due to both aromatic and olefinic sp$^2$ carbon, but the shoulder at 1630 cm$^{-1}$ is unambiguously assigned to the C = C stretching modes of olefinic compounds (Figure 5(b)) (Socrates 2001; Gaiván et al. 2017). The presence of olefinic moieties is further confirmed by the characteristic wagging modes of olefins at 988 and 910 cm$^{-1}$ (Socrates 2001). The band at 1074 cm$^{-1}$ might be due to the CH$_2$ rocking mode characteristic of vinyl groups, in accordance with the observation of styrene (and maybe also vinylnaphthalene) by mass spectrometry, though the aromatic in-plane CH bending modes overlap in this region.

The broad band that appears in the 1800–1000 cm$^{-1}$ region is characteristic of amorphous carbon and its intensity is related to the relative amount of sp$^2$ to sp$^3$ carbon hybridization (Ferrari et al. 2003; Rodil 2005). Its presence in the IR spectrum is consistent with the amorphous morphology observed by TEM and suggests that part of the dust analogs are made of amorphous carbon material.

Finally, weak C = O carbonyl stretching bands are observed, which we consider as related to the acetone impurity in the C$_2$H$_2$ bottle since the base pressure of the Stardust machine is $10^{-10}$ mbar and the sample was transferred to the IR UHV chamber by means of a UHV suitcase at a pressure lower than $5 \times 10^{-9}$ mbar.

In addition, we have tested the stability of the analogs after air exposure and observed that they show a high reactivity (Figure 6), whereas we did not observe any significant change in the IR spectrum of the analogs after 24 hr in UHV. Carbonaceous materials produced from unsaturated precursors are known to react swiftly with oxygen, leading to the formation of C–O–C moieties. Mainly, we have observed the incorporation of oxygen through the increase of the carbonyl C = O stretching modes and through the appearance and growth of a band at 1250 cm$^{-1}$, assigned to the C–O–C stretching mode. In addition we have observed a reduction in
desorption. Other volatile species detected by in situ mass spectrometry, such as benzene or toluene, were not detected by LDI-MS despite the high sensitivity of the technique to aromatics (Sabbah et al. 2017). C$_{6}$H$_{4}$ could be identified, which was also detected by in situ mass spectrometry and is an important molecule for the formation of benzene. Moreover, C$_{2}$H$_{2}$ and C$_{3}$H$_{2}$ are believed to be produced during the laser desorption stage from the common C$_{3}$H$_{2}$ precursor (see the supplementary material in Martínez et al. 2020).

On the other hand, C- and HC-clusters with carbon atoms from 5 to 20 dominate the mass spectrum, with C$_{5}$H and C$_{11}$ particularly abundant. Relatively large aromatics are also present in the dust analog from C$_{12}$H$_{8}$ (acenaphthylene) to C$_{20}$H$_{12}$. Finally, the peaks assigned to C$_{3}$HO and C$_{7}$HO evidence oxidation of the sample likely due to air exposure. The results from LDI-MS are summarized in Figure 7(b) by using a double bond equivalent (DBE) analysis. Briefly, in the case of hydrocarbons, DBE can be defined as the sum of the number of double bonds involving carbon plus the number of rings for a particular species. A description of the DBE analysis can be found in, e.g., Sabbah et al. (2017), Gavilan et al. (2020), and in the supplementary information of Martínez et al. (2020). Three molecular families, namely aromatics, HC-, and C-clusters, were considered and their relative intensities in terms of summed peak intensities are shown.

4. Discussion

4.1. Formation of Polyacetylenic Chains (C$_{2n}$H$_{2}$)

Linear polyacetylenic chains, C$_{2n}$H$_{2}$, are observed in the outer layers around C-rich stars and their formation involves the ethynyl radical (C$_{2}$H), which is formed by the photodissociation of C$_{2}$H$_{2}$ in the outer layers of the CSE and triggers the chemistry of linear polyacetylenic chains (Cernicharo 2004; Agúndez et al. 2017). Once the C$_{2}$H radical is formed, the formation of polyacetylenes proceeds mainly through reactions of the type

$$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H \quad (R1)$$

which are assumed to occur fast at low temperatures (see the scheme in Figure 8) (Chastaing et al. 1998; Agúndez et al. 2017). A second important chemical route for the formation of triacetylene and larger polyacetylenic chains involves the radical C$_4$H through reactions of the type (Berteloite et al. 2010; Agúndez et al. 2017)

$$C_4H + C_{2n}H_2 \rightarrow C_{2n+4}H_2 + H. \quad (R2)$$

Besides the photodissociation of diacetylene, the C$_{4}$H radical can be efficiently formed by the interaction with dicarbon through the bimolecular reaction

$$C_2 + C_2H_2 \rightarrow C_4H + H. \quad (R3)$$

In CSEs around C-rich AGB stars, the interaction of C$_2$H$_{2}$ with energetic radiation can lead to dissociation but also to
ionization. Taking into account that ion–neutral reactions are usually faster than neutral–neutral reactions (e.g., the rate constant of $\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2$ is 2.5–5 times higher than that of $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3 + \text{H}_2$; Anicich 1993; Chastaing et al. 1998), chemical reactions involving ions may also play a role in the synthesis of polyacetylenic chains. The polymerization of $\text{C}_2\text{H}_2$ in the external layers is dominated by neutral–neutral reactions involving $\text{C}_2\text{H}_2$, rather than by ion–molecule reactions involving $\text{C}_2\text{H}_2^+$, because photodissociation of $\text{C}_2\text{H}_2$ by the interstellar UV field is 5–10 times faster than photoionization (Heays et al. 2017; Agúndez et al. 2018). However, in the inner clumps of CSEs, where dust acts as an efficient shield against UV photons but cosmic rays can penetrate, some $\text{C}_2\text{H}_2$ may be chemically processed due to cosmic-ray-induced ionization and further ion–molecule reactions. The C-star envelope IRC +10216 is known to present a clumpy structure (Cernicharo et al. 2015) and, in fact, cation–neutral reactions have been suggested to play a role for the formation of, e.g., $\text{CH}_3\text{CN}$, $\text{SiH}_3\text{CN}$, and $\text{CH}_2\text{SiH}_3$ (Agúndez et al. 2008; Cernicharo et al. 2017). However, the measured abundances of ions (cations and anions) is very low ($X \approx 10^{-10}$), precluding an important role in the chemistry of the most abundant carbon-bearing species (note that the anions of all $\text{C}_2\text{H}$ radicals have been detected in the external, cold layers of the envelope but not in the inner, warm regions).

In our experiments, as mentioned in the previous section, we estimate that around 2% of the injected acetylene reaches the magnetron and can therefore be dissociated into $\text{C}_2\text{H}$ by electron impact (see Figure 9 for a scheme on the formation mechanism of radicals from atomic carbon and acetylene in the SGAS). The interaction of $\text{C}_2$ with $\text{H}_2$ (either residual in the chamber as well as produced by recombination of the atomic hydrogen in excess) contributes also to the formation of the $\text{C}_2\text{H}$ radical via the bimolecular reaction $\text{C}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H}$ (Cernicharo 2004; Martínez et al. 2020). In addition, and due to the higher cross section for electron impact ionization over electron impact dissociation (Mao et al. 2008), chemical reactions involving cations such as $\text{C}_2\text{H}_2^+$ and $\text{C}_2\text{H}_3^+$ might take place. However, the electron temperature of the plasma in magnetron sputtering discharges and in SGASs is lower than 10 eV (Ivanov et al. 1992; Kousal et al. 2017), which favors electron impact dissociation over direct ionization or dissociative ionization events. This is different to the case of dusty plasmas in which apart from the neutral dissociative production of $\text{C}_2\text{H}$, there is a higher probability for the formation of $\text{C}_2\text{H}_2^+$ (from $\text{C}_2\text{H}_2$) and $\text{C}_2\text{H}_3^+$ (from $\text{C}_2\text{H}_3$) by electron knocking-off and dissociative ionization processes, respectively. Thus, the chemistry of the formation of NPs in $\text{C}_2\text{H}_2$ dusty plasmas presents a nonnegligible ion–neutral contribution (Jiménez-Redondo et al. 2019). In addition, anionic polymerization routes can be relevant in acetylene plasmas (Deschenaux et al. 1999; De Bleecker et al. 2006b; Jiménez-Redondo et al. 2019) due to the trapping of negative ions in the plasma potential, despite the electron attachment probability being several orders of magnitude lower than those for electron impact dissociation/ionization. However, the chemistry involving anions is very unlikely in SGASs, in which it has been shown that the chemistry proceeds predominantly by neutral–neutral interactions (Haberland et al. 1991; Martínez et al. 2020).

On the other hand, the results from OES suggest that the excited $\text{C}_2$ is consumed to some extent in the reaction (R3) to produce the $\text{C}_4\text{H}$ radical. Therefore, during the production of the dust analogs the growth of polyacetylenic chains involves mainly the $\text{C}_2\text{H}$ and $\text{C}_4\text{H}$ radicals (Figure 8). Moreover, the incorporation of conjugated polyalkynes to the dust analogs in higher amounts than those observed in acetylene discharges, as probed by IR spectroscopy, supports a significant contribution of the $\text{C}_2\text{H}$ chemical route, which is initiated by the addition of atomic carbon and subsequent formation of $\text{C}_2$ in substantial amounts.

All the abovementioned reactions leading to the growth of polyacetylenic chains release either atomic or molecular hydrogen, which is consistent with the observed increase in the peak at $m/z = 2$ (Figure 3(c)) and with the increase of the $\text{H}_2$ line in the optical emission spectra (Figure 2(a)), being therefore available in high amounts to participate in further chemical reactions. We assume that the atomic hydrogen that is not consumed in chemical reactions is recombined into $\text{H}_2$ by three-body reactions involving both Ar and the solid dust analogs.

4.2. Formation of PAHs

Benzene formation is considered as the bottleneck for the growth of PAHs, which have been proposed as the carriers of the AIBs and the seeds of carbonaceous cosmic dust. Benzene has been detected in PPNe (Cernicharo et al. 2001b; Malek et al. 2011) but not yet in the CSE of C-rich AGB stars, which constitute the main factories of cosmic dust. In addition, no specific PAH structure has been identified from observations. In particular, the apolar (or weakly polar) character of these molecules, along with large rotational partition functions, hinder its detection by rotational emission spectroscopy (e.g., Joblin & Mulas 2009). Recently, benzonitrile has been detected in the ISM (McGuire et al. 2018), whose formation might be linked to cyanopolyynes in the same manner as benzene is believed to be related to polynes.

Despite the lack of successful detection of benzene or PAHs in CSEs around C-rich AGB stars, a bottom-up chemical pathway, derived from combustion experiments, has been proposed for the formation of benzene and PAHs in the warm inner regions of C-rich CSEs (Cherchneff et al. 1992; Cherchneff 2012). In this scheme, the key reaction is the direct recombination of two propargyl radicals to form both

Figure 9. Formation mechanism of radicals from atomic carbon and acetylene in the SGAS. Molecular hydrogen is both residual in the ultrahigh vacuum system and formed by recombination of the released atomic hydrogen.
cyclic and linear \( C_6H_6 \) as well as the phenyl radical \((C_6H_5)\):

\[
C_3H_3 + C_3H_3 \rightarrow C_6H_6 \quad \text{(R4a)}
\]

\[
C_3H_3 + C_3H_2 \rightarrow C_6H_5 + H \quad \text{(R4b)}
\]

reaction (R4a) being more efficient than (R4b). A different chemical scheme involving hydrocarbon ions has been proposed to explain the formation of benzene in the protoplanetary nebula CRL 618 (Woods et al. 2002), where \( C_6H_6 \) has been detected. In this scheme, the synthesis is initiated with proton transfer to \( C_2H_2 \) to form \( C_2H_3 \), followed by successive reactions with \( C_2H_2 \) to form cyclic \( C_6H_5 \), and ending with the reaction of \( C_6H_5 \) with \( H_2 \) to form \( C_6H_6 \), which yield benzene upon dissociative recombination with electrons.

Apart from a top-down etching process (Merino et al. 2014) not considered here, another possible bottom-up mechanism for the formation of benzene involving neutral–neutral reactions has been derived from plasma discharges (De Bleecker et al. 2006a). In this case, \( C_3H_2 \), which is also crucial to the formation of polyacetylenic chains, initiates the chemistry mainly by the termolecular association reaction

\[
C_2H + C_2H_2 + M \rightarrow C_4H_3 + M. \quad \text{(R5)}
\]

where \( M \) stands for a third body.

In our case, due to the temperatures involved in the sputtering process in the SGAS (in the order of 500 K) we rule out the formation of benzene via propargyl radicals (note that the \( C_3H_3 \) observed by LDI-MS is formed during the laser desorption step by protonation of \( C_3H_2 \)). In fact, the concurrent detection of \( C_6H_4 \) and \( C_6H_5 \) by in situ mass spectrometry points toward a similar neutral–neutral route as that proposed for \( C_2H_2 \) discharges, involving \( C_2H \) and the formation of the butadienyl radical \((C_4H_3)\). Moreover, the formation of \( C_4H_3 \) is less efficient than that of \( C_4H_2 \), which explains the observation of \( C_4H_6 \) only at the higher \( C_2H_2 \) flows in our experiments. Once \( C_3H_3 \) is formed, the main reactions with \( C_2H_2 \) produce \( C_5H_3 \) and \( C_6H_4 \) (Figure 10), which account for about 75% and 25% of the reaction mechanism toward \( C_6H_6 \), respectively (De Bleecker et al. 2006a). In our case, the detection of \( C_6H_3 \) is hindered due to the location of the mass spectrometers, which only allows stable species to be detected.

Once \( C_6H_6 \) is formed, the growth toward PAHs has been considered in astrophysical models to proceed by the so-called HACA mechanism in which acetylene is the main species propagating the growth of aromatic rings (Figure 10). In addition, the HAVA mechanism (Zhao et al. 2018) and fusion of PAHs (Shukla & Koshi 2010) have been proposed for the growth of large benzooid PAHs. However, none of them explains the formation of aromatics with aliphatic substituents (except those of acetylenic nature), such as those observed in our experiments, both in the gas phase (by in situ mass spectrometry) and in the solid dust analogs (by in situ IR spectroscopy).

4.3. Formation of Alkyl-substituted Aromatics

Alkyl-substituted aromatics have been proposed to be present in space based on the analysis of the \( 3.3/3.4 \mu m \) band intensity ratio (Joblin et al. 1996). Li & Draine (2012) estimated an upper limit of around 15% for the aliphatic fraction in PAHs derived from the intensities of the 3.4 and 6.85 \( \mu m \) emission features. The formation of alkyl-substituted aromatics is expected to involve the reactivity of the methyl radical \((CH_3)\) with aromatic units and/or aromatic radicals (Shukla et al. 2010).

In CSEs around C-rich AGB stars, \( CH_4 \) has been detected (Keady & Ridgway 1993) and it is likely that methyl radicals are present, although they have not been detected and their abundance is unknown. Chemical equilibrium predicts a relatively low abundance of \( 10^{-9} \) relative to \( H_2 \) in the stellar atmosphere (Agúndez et al. 2020), and unfortunately chemical kinetics models of the inner wind (e.g., Cherchneff 2012) have not provided abundance estimates for \( CH_4 \). A bottom-up synthesis of \( CH_3 \) must involve the methylidyne radical \( (CH) \), which might arise from the interaction of atomic carbon with molecular hydrogen via \( C + H_2 \rightarrow CH + H \). However, this reaction is endothermic by about 100 kJ mol\(^{-1}\) and necessitates temperatures in the range of several thousand kelvin to be efficient. Thus, shock-wave-induced chemistry would be needed to efficiently form the methylidyne radical from a bottom-up approach. Once \( CH \) radicals are formed, the interaction with \( H_2 \) through the reaction

\[
CH + H_2 + M \rightarrow CH_3 + M \quad \text{(R6)}
\]

where \( M \) stands for a third body, can lead to \( CH_3 \). If this is the case, cosmic dust might be needed as third body to efficiently produce \( CH_3 \). On the other hand, \( CH_3 \) radicals can be formed in the outer layers of the CSE by photodissociation of \( CH_4 \) in the same way as \( C_2H \) radicals are formed from \( C_2H_2 \).

Methylated species have been detected in the C-star AGB IRC+10216 (Cernicharo et al. 2000, 2017; Agúndez et al. 2015). However, their low abundances suggest that they play a minor role in the chemistry of the envelope. A different situation has been found in the CRL618 PPN, where methylpolyynes \((CH_3C_2H\) and \( CH_3C_4H\)) have been detected with abundances much larger than those observed in IRC +10216 (Cernicharo et al. 2001a).

Aromatic compounds with aliphatic moieties are neither produced in acetylene pyrolysis (Shukla & Koshi 2012) nor detected (or only very marginally) as neutral species in the gas phase of acetylene discharges (Deschenaux et al. 1999; Consoli et al. 2008). However, this is drastically different when other hydrocarbons are used, particularly in ethylene pyrolysis and ethylene plasmas (Jäger et al. 2006; Gillon & Houssiau 2014). This is related to the formation of alkyl radicals which enter into the chemistry, thus promoting the formation of alkyl moieties. Shukla et al. (2010) demonstrated that pyrolysis of aromatics in the presence of \( CH_3 \) radicals can lead to aromatic growth through a methyl-addition cyclization process and Gavilan et al. (2020) have recently proposed a route for PAH growth at low temperatures (150–200 K) by the addition of alkyl radicals.
In our case, the CH radical, which we observe by OES, is formed by the reaction
$$C + H + Ar/dust \rightarrow CH + Ar/dust \quad (R7)$$
involving Ar and the solid dust analogs as third body.

Once the CH radical is formed, subsequent three-body associations with atomic H would lead to CH$_3$. This chemical route continues to the formation of CH$_4$, but the acetone impurity in the C$_2$H$_2$ bottle prevents its detection by in situ mass spectrometry. Nevertheless, we have recently demonstrated the formation of CH$_4$ and C$_2$H$_4$ by the interaction of atomic C and H$_2$ even at very low H$_2$ concentrations (Martínez et al. 2020).

The formation of toluene (C$_7$H$_8$) proceeds then by the reaction of phenyl (C$_6$H$_5$) and methyl (CH$_3$) radicals through
$$C_6H_5 + CH_3 \rightarrow C_7H_8 + H \quad (R8)$$
the phenyl radical being formed as shown in Figure 10.

The growth toward longer alkyl-chain substitutions to form, e.g., ethylbenzene (C$_8$H$_{10}$) proceeds through hydrogen abstraction and methyl addition. This process is not limited to the phenyl radical but applies to any other aromatic radical formed during the growth of PAHs through the HACA mechanism (e.g., naphtyl: C$_{10}$H$_7$, acenaphtyl: C$_{12}$H$_7$, …) and provides a route for the growth of alkyl-substituted PAHs (Figure 11), closely related to the methyl-addition cyclization mechanism (Shukla et al. 2010).

On the other hand, the likely detection of styrene (C$_8$H$_8$) (maybe vinylnaphthalene (C$_{11}$H$_{10}$) as well) by in situ mass spectrometry (including a band likely related to vinyl moieties) points toward the production of the vinyl radical (C$_2$H$_2$). Bimolecular reactions involving C, C$_2$H$_2$, and H$_2$ to form C$_2$H$_3$ are highly endothermic for all the possible chemical routes. The same holds for the addition of C$_2$H$_3$ to PAHs and aromatic radicals. Therefore, we assume that the formation of aromatics with vinyl substitutions proceeds by three-body reactions involving both Ar and the solid dust analogs.

4.4. Formation of C-clusters with Odd-C Atoms

Molecules and carbon clusters with odd numbers of carbon atoms have been detected in the circumstellar environments of C-rich stars (Hinkle et al. 1988; Bernath et al. 1989) as well as in interstellar clouds (Maier et al. 2001). However, the growth of carbon clusters from C and C$_2$ at the temperatures found in the CSE is still not well characterized since most chemical reactions involving small C-clusters are still unknown. To date only the C$_2$+C$_2$ reaction has been measured at high temperature (Kruse & Roth 1997), and has been shown to present a high reaction rate. Therefore, although it potentially contributes to the chemistry, much is yet to be understood about the role of the C$_n$+C$_m$ reactions in the formation of large C-clusters. An alternative and efficient chemical route is provided by the interaction of atomic carbon with C$_2$H$_2$ through the reactions (Cernicharo 2004)
$$C + C_2H_2 \rightarrow C_2H + H \quad (R9a)$$
$$C + C_2H_2 \rightarrow C_3 + H_2 \quad (R9b)$$
Additionally, C$_2$H again plays an important role, as in the formation of polycyclic chains and benzene, as well as C$_4$H by the interaction with atomic carbon via
$$C + C_2H \rightarrow C_3 + H \quad (R10a)$$
$$C + C_2H \rightarrow C_4 + H \quad (R10b)$$

Once C$_3$ and C$_5$ are formed by (R9) and (R10), the growth toward larger molecules with odd numbers of carbon atoms proceeds through the following reactions with acetylene:
$$C_{2n+1} + C_2H_2 \rightarrow C_{2n+3}H + H \quad (R11a)$$
$$C_{2n+1} + C_2H_2 \rightarrow C_{2n+3} + H_2 \quad (R11b)$$
as well as by the following interactions with C$_4$H and C$_6$H:
$$C_{2n+1} + C_4H \rightarrow C_{2n+3} + H \quad (R12a)$$
$$C_{2n+1} + C_4H \rightarrow C_{2n+5} + H \quad (R12b)$$

Therefore, the growth of C-clusters with odd numbers of carbon atoms proceeds through two different chemical routes: an acetylenic route (R11) and a radical route (R12). In fact, these two chemical pathways do not apply only to C$_{2n+1}$-clusters but also to C$_{2n}$-clusters, providing a chemical path to the formation of hydrogenated C-clusters.

The abovementioned mechanisms necessitate atomic carbon to initiate the chemistry, which is not present in acetylene combustion experiments or in acetylene discharges. In fact, in particle-forming acetylene discharges the dominant species are by far hydrocarbon molecules with even numbers of carbon atoms (Deschenaux et al. 1999; Kovačević et al. 2003; Consoli et al. 2008; Benedikt 2010). In contrast, the supply of atomic carbon in our case opens up both the acetylenic and the C$_2$H/C$_4$H radical routes described, resembling more closely the mechanism operating in the CSEs of C-rich stars. Figure 12 summarizes the chemical network for the growth of C-clusters. Three-body reactions involving Ar, which cannot be excluded in our experiments, are also shown.

5. Conclusions

In this paper we present a thorough study of the gas-phase chemistry of acetylene in the presence of C and C$_2$ which can
pertain to the outer layers of C-rich AGB stars and PPNs. We have formed and studied in situ cosmic dust analogs employing atomic carbon and acetylene as precursors, using a well-controlled ultraclean experimental setup. Apart from the formation of linear polyacetylenic chains, we have observed the formation of PAHs. More importantly, aromatics with aliphatic substitutions as well as pure and hydrogenated carbon clusters were produced as a direct consequence of the addition of atomic carbon. The growth of carbon clusters proceeds from atomic carbon and acetylene as precursors, using a well-supported mechanism. In addition, the observed gas-phase species incorporate into the dust analogs, which consist of a complex mixture of sp, sp², and sp³ hydrocarbons with an amorphous morphology. Our results are of particular interest for unveiling chemical routes leading to formation of acetylene-based molecular species in the external layers of AGB stars and in PPNs, and to foster the search for alkyl-substituted aromatics in these environments.

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