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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are omnipresent in the Interstellar Medium (ISM) and also in carbonaceous meteorites (CM) such as Murchison. However, the basic reaction routes leading to the formation of even the simplest PAH – naphthalene (C₁₀H₈) – via the Hydrogen-Abstraction/Acetylene-Addition (HACA) mechanism still remain ambiguous. Here, by untwining the uncharted fundamental chemistry of the styrenyl (C₇H₅) and the ortho-vinylphenyl radicals (C₉H₅) – key transient species of the HACA mechanism – with acetylene (C₂H₂), we provide the first solid experimental evidence on the facile formation of naphthalene in a simulated combustion environment validating the previously postulated HACA mechanism for these two radicals. This study highlights, at the molecular level spanning combustion and astrochemistry, the importance of the HACA mechanism to the formation of the prototype PAH naphthalene.

For more than three decades, the formation of polycyclic aromatic hydrocarbons (PAHs) – organic molecules carrying fused benzene rings – in extreme environments has remained a highly controversial topic.[3-6] Accounting for up to 20% of the cosmic carbon budget and linked to the prebiotic evolution of the interstellar medium,[5,7] the ubiquitous presence of PAHs in the interstellar space has been implied from the diffuse interstellar bands (DIBs) – discrete absorption features ranging from the blue part of the visible (400 nm) to the near-infrared (1,200 nm) overlaid well with the interstellar extinction curve.[8-11] – and via the unidentified infrared (UIR) emission bands probed in the range of 3 to 14 μm.[10,12-13] The identification of PAHs in carbonaceous chondrites such as Murchison along with C¹³C isotopic studies convincingly support an interstellar origin.[14] Based on extensive combustion models, it is recommended that the Hydrogen-Abstraction/Acetylene-Addition (HACA) mechanism dictates the synthesis of PAHs not only in sooting combustion flames, but also in circumstellar envelopes of dying Asymptotic Giant Branch (AGB) stars such as IRC+10216.[2,4,10-16] Here, the HACA route assumes a recurring sequence via abstraction of a hydrogen atom from the reacting aromatic hydrocarbon followed by addition of an acetylene molecule (C₂H₂) to the radical site. Commencing with benzene (C₆H₆), this pathway leads first to the phenyl radical (C₆H₅) pursued by addition of the acetylene molecule yielding the styrenyl radical (C₇H₅) (Scheme 1). The addition of the second acetylene molecule is suggested to proceed either to the styrenyl radical or to the ortho-vinylphenyl radical (C₉H₅), which is formed via isomerization of the styrenyl species. Subsequent cyclization and atomic hydrogen loss accompanied by aromatization was proposed to finally yield naphthalene (C₁₀H₈) – the simplest PAH – at temperatures up to 1,000 K.[3] However, although naphthalene has been revealed experimentally as an overall product of the reaction of the phenyl radical with two acetylene molecules,[15] the underlying elementary reactions of the styrenyl and of the ortho-vinylphenyl radicals with acetylene leading to naphthalene have never been explored experimentally. From the historical viewpoint, the synthesis of styrene itself was studied by Berthelot in 1867.[16] Later, acetylene was suggested to first dimerize to vinylacetylene subsequently adding another acetylene to form 1,3-hexadien-5-yne.[17] The latter was found to cyclize primarily to (1,2,4)cyclohexatriene[18] – an intermediate ultimately leading to benzene and styrene.[19] Since combustion models are essentially troubled with likely reaction pathways to PAH synthesis, detailed studies driving the PAH formation such as via styrenyl and ortho-vinylphenyl have remained largely speculative, and even the fundamental formation mechanism of the prototype PAH – the naphthalene molecule – within the framework of the HACA mechanism has remained elusive to date.

Here, we untangle experimentally the hitherto unexplored fundamental chemistry of the styrenyl and ortho-vinylphenyl radicals, the key transient species in the HACA mechanism, which have been suggested to lead to the formation of the naphthalene molecule via reaction with acetylene. Conducted in a simulated combustion environment, this study provides the first explicit experimental evidence that the naphthalene molecule represents the key reaction product in both systems. The exclusive pathways to naphthalene synthesis unequivocally establish fundamental mass growth processes from styrenyl and ortho-vinylphenyl radicals to naphthalene via acetylene addition followed by isomerization, hydrogen elimination, and aromatization. The unique benefits of fragment-free photoionization exploiting tunable vacuum ultraviolet (VUV) light in tandem with the detection of the photoionized molecules by a Reflectron Time-of-Flight Mass Spectrometer (ReTOF-MS) as exploited here to provide evidence in the elucidation of

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Supporting Information and the ORCID identification numbers for the authors of this article can be found under XXX.
the fundamental, elementary reaction mechanisms forming naphthalene within the framework of the HACA mechanism not only in combustion flames, but also in more exotic environments like circumstellar envelopes of aging carbon stars.

The naphthalene molecule was formed via a directed synthesis of the styrenyl and of the ortho-vinylphenyl transients with acetylene in a high temperature chemical reaction, respectively (Materials & Methods, Supporting Information). In brief, the styrenyl and the ortho-vinylphenyl radicals were generated via pyrolysis of β-bromostyrene and 2-bromostyrene (C₆H₄Br), respectively. These precursors were seeded in neat acetylene at 400 Torr and expanded into a resistively-heated silicon carbide (SiC) tube (‘chemical reactor’) kept at 1,500 ± 50 K. The acetylene served as both seed and reactant gas with the pyrolytically generated radicals. The benefit of this setup is the capability of identifying the reaction products in situ within the molecular beam after passing the skimmer downstream with respect to the heated nozzle. The neutral molecular beam was intersected by the tunable vacuum ultraviolet (VUV) light in the extraction region of a Wiley–McLaren Reflectron Time-of-Flight Mass Spectrometer (Re-TOF-MS), and the photoionized molecules were then sampled by a microchannel plate (MCP) detector. Mass spectra were collected at an interval of 0.05 eV between 8.00 eV and 11.00 eV. Control experiments, in which acetylene was replaced by helium, were also conducted.

Figure 1 shows typical mass spectra recorded at a photoionization energy of 9.50 eV for styrenyl in acetylene (Figure 1a) and ortho-vinylphenyl in acetylene systems (Figure 1b); reference spectra obtained by replacing the acetylene reactant with helium carrier gas are also presented in Figures 1c and 1d. For both the styrenyl and the ortho-vinylphenyl reactants, a comparison of the acetylene with the helium seeded systems reveals fascinating findings. All mass spectra are dominated by signal from mass-to-charge ratio (m/z) of 102 to 104. The ion counts at m/z 104 and 102 originate from C₆H₅⁺ and C₅H₆⁺, respectively. Signal at m/z 103 could account for C⁵⁺C₆H₅⁺ at levels of up to 9 % with respect to C₆H₅⁺, along with C₅H₆⁺, i.e. the photoionized styrenyl and ortho-vinylphenyl radicals. Note that all spectra depict signal at m/z 182 and 184, which stem from the photoionized, non-pyrolyzed C₅H₅Br and C₅H₆Br precursors, respectively. These ion counts are common to all helium and acetylene seeded systems and, therefore, do not originate from bimolecular reactions between the styrenyl/ortho-vinylphenyl radicals with acetylene. Experiments with pure acetylene did not reveal signal beyond m/z 30, which agrees well with the findings by Parker et al.⁶ On the other hand, signal at m/z 128 and 126 are unique to the acetylene-seeded styrenyl and ortho-vinylphenyl systems (Figures 1a and 1b). As a consequence, products of the chemical formula C₅H₅ (128 amu) and C₅H₆ (126 amu) must relate to reaction products between the styrenyl/ortho-vinylphenyl radicals and acetylene. More specifically, the C₅H₆ product (128 amu) is synthesized via the reaction of the C₅H₅ radical (103 amu) with a single acetylene molecule (C₂H₂: 26 amu) accompanied by the emission of one hydrogen atom (Scheme 1; reaction (1)). Therefore, the analysis of the raw data alone delivers compelling evidence that in the reactions of the styrenyl/ortho-vinylphenyl radicals with acetylene, hydrocarbon isomer(s) of the molecular formula C₅H₅ is (are) formed in both systems.

(1) \[ C₂H₂ + C₅H₅ \rightarrow C₅H₆ + H \]

Figure 1. Mass spectra recorded at a photoionization energy of 9.50 eV for species formed via the styrenyl in acetylene (a) and ortho-vinylphenyl in acetylene systems (b). Spectra for acetylene replaced with helium are shown in (c) and (d), respectively. Key product isomers are labelled in red and green. Ions from acetylene and helium originate from higher harmonics.

However, which isomer is formed? To identify the nature of the product isomer(s), we switch our focus to the analysis of the photoionization efficiency (PIE) curves, which report the intensities of
the ions at m/z 128 (C_{10}H_{23}) as a function of the photon energy (Figure 2). The experimentally recorded PIE curves can then be compared with known PIE curves from the database for distinct isomers of C_{10}H_{23}. Here, the experimental data as displayed in black can be reproduced exceptionally well with the reference PIE curve of naphthalene[24-26] superimposed in red for both the styrenyl and ortho-vinylphenyl in acetylene systems. We also investigated the reference PIE curves of the alternative isomers like azulene (C_{10}H_{8}). However, the PIE curve of azulene does not replicate the experimental data; the onset of the reference PIE curve of azulene starts at 7.44 ± 0.03 eV,[26] which is about 0.7 eV lower than our experimental onset of 8.14 eV and the reference ionization energy (IE) of naphthalene of 8.1442 ± 0.0009 eV.[27] We would like to highlight that the PIE curve of C_{10}H_{15} is unique to each molecule indicating that the existence of other isomers in the molecular beam would change the shape of the PIE curves considerably. Therefore, we determine that naphthalene represents the sole contribution to signal at m/z 128. For completeness, it should be noted that a detailed inspection of the PIE curves at m/z 102 to 104 (Supporting Information) suggests the formation of phenylacetylene (C_{8}H_{16}) 102 amu; 8.81 eV (exp.); IE = 8.825 ± 0.001 eV[28]) and of styrene (C_{8}H_{12}) 104 amu; 8.45 eV (exp.); IE = 8.464 ± 0.001 eV[29]) possibly via hydrogen atom loss and addition to the styrenyl (C_{8}H_{13}) 103 amu) and ortho-vinylphenyl (C_{8}H_{13}) 103 amu) radicals, respectively.[16] The PIEs at m/z 103 could be reproduced with solely 13C-substituted phenylacetylene (13C_{8}H_{16}; 103 amu; 8.81 eV (exp.); IE = 8.825 ± 0.001 eV[28]). This finding suggests that once formed, the styrenyl and ortho-vinylphenyl radicals do not survive within the chemical reactor, but rather decompose via atomic hydrogen loss/addition to phenylacetylene/styrene or react with acetylene to form eventually naphthalene under our experimental conditions.[16] Note that theoretical statistical (RRKM/Master Equation) calculations[26] at the experimental conditions of 1,500 K and 400 Torr reveal that the styrenyl radical equilibrates with the phenylacetylene plus atomic hydrogen and/or with ortho-vinylphenyl. The bimolecular rate constants for the reactions of styrenyl and ortho-vinylphenyl radicals with acetylene at these conditions were computed as 1.2×10^{-12} and 1.5×10^{-15} cm^3 molecule^{-1} s^{-1}. Taking the concentration of acetylene as 1.4×10^{-3} molecule cm^{-3} from the ideal gas law, we then obtain pseudo-first order rate constants for the reaction of acetylene as 1.7×10^{11} and 2.1×10^{11} s^{-1} for styrenyl and ortho-vinylphenyl, respectively. Clearly, at these conditions the bimolecular reactions with acetylene should be much faster than unimolecular decomposition of styrenyl and ortho-vinylphenyl[16] therefore the C_{8}H_{15} radicals are expected to be fully consumed during the residence time of a few tens of microseconds[30-31] in the chemical reactor. The PIE curve at m/z 126 might originate from the diethynylbenzene isomers (Supporting Information).

Our experiments demonstrate convincingly for the first time that the naphthalene molecule is synthesized in the pyrolytic reactor under combustion-like conditions via the reactions of the styrenyl/ortho-vinylphenyl radicals with acetylene involving the HAQA routes as compiled in Scheme 1. Here, the reactions are initiated by addition of acetylene to styrenyl/ortho-vinylphenyl via barriers of 24 and 17 kJ mol^{-1}; the collision complexes were found to be bound by 155 and 162 kJ mol^{-1} with respect to the separated reactants[16] and undergo ring closure to form two distinct, singly hydrogenated naphthalene isomers (Scheme 1). The reaction terminates via unimolecular decomposition by hydrogen atom emission from the bridging carbon and β-carbon atoms, respectively, eventually leading to the formation of naphthalene via exit barriers of 48 and 26 kJ mol^{-1} above the separated products.[16] The observation of the m/z 126 peak (C_{10}H_{23}) in the acetylene seeded β-bromostyrene system might be attributed to the formation of naphthylene (didehydrodihydronaphthalene) via the Frenklach sequence[28] or to diethynylbenzenes. The styrenyl radical is less stable than ortho-vinylphenyl and hence produces a larger amount of phenylacetylene (C_{8}H_{15}) as evidenced by the stronger m/z 102 peak (Figure 1). A fraction of phenylacetylene molecules can be activated by intermolecular hydrogen atom abstraction (e.g. by hydrogen atoms generated in the system) from the ortho position in the ring and the resulting C_{8}H_{15} radical can react with acetylene eventually producing naphthylene after ring closure and hydrogen atom elimination.[29] If the atomic hydrogen loss occurs prior to the ring closure, 1,2-diethynylbenzene can be produced. The naphthyl radical, which can be also formed in the C_{8}H_{15} reaction with acetylene, can yield naphthalene by hydrogen atom addition. Alternatively, if the atomic hydrogen abstraction takes place from meta- or para- positions in phenylacetylene, the reactions of the resulting C_{8}H_{15} radicals with acetylene can produce 1,3- and 1,4-diethynylbenzenes, respectively, by acetylene addition/H elimination.

The overall facile synthesis routes to naphthalene via the reactions of styrenyl and ortho-vinylphenyl with acetylene provide compelling evidence for the legitimacy of the HACA mechanism under combustion-like conditions. This mechanism leads to aromatization and PAH synthesis from a single, monocyclic aromatic species at elevated temperatures as present in the combustion

![Figure 2. Photoionization efficiency (PIE) curves recorded at m/z 128 in the styrenyl with acetylene (a) and ortho-vinylphenyl with acetylene (b) systems. The black line shows the experimental curve with the uncertainty defined as the gray area. The red lines indicates the reference PIE curve for naphthalene.](image-url)
flames and also in more exotic environments such as in circumstellar shells of dying carbon stars close to their photosphere. We acknowledge that the outcome of every chemical reaction is influenced by the temperature and pressure. Consequently, the detection of naphthalene at only one set of physical parameters (1,500 K, 400 Torr) does not afford a comprehensive picture of the complete HACA mechanism and how the reaction products quantitatively change over an extended range of temperatures and pressures. In the meantime, the unambiguous expression of the HACA pathways along with the detection of the prototypical PAH – naphthalene – exploiting single-photon ionization mass spectrometry signifies a robust framework for high-temperature models of combustion systems and of circumstellar envelopes of carbon stars as postulated by Frenklach three decades ago.

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