Hydrogen Abstraction – Acetylene Addition Exposed!

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(PAHs) along with their hydrogenated and ionized counterparts are omnipresent in carbonaceous meteorites (CM) such as Murchison and in the interstellar medium (ISM). However, the basic reaction mechanisms leading to the formation of even the simplest PAH – naphthalene (C10H8) – via the hydrogen abstraction-ace­ty­lene addition (HACA) mechanism is still elusive. Here, by untangling the hitherto unexplored fundamental chemistry of the sty­re­­n­yl (C8H7) and of the ortho-vinylphenyl radicals (C8H7) – the key transient species of the HACA mecha­ni­sm – with the acetylene molecule (C2H2), we provide the very first experimental evidence on the facile formation of naphthalene (C10H8) in a simu­la­ted combustion environment and hence the legitimacy of the HACA mechanism, which previously had only been hypothesized theoretically. This study eventually provides the manifestation and importance of the HACA mechanism on the molecular level spanning combustion science and astrochemistry.

 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.[1-4](#_ENREF_1" \o "Frenklach, 1985 #535) Accounting for up to 20% of the cosmic carbon budget and linked to the prebiotic evolution of the interstellar medium,[5-7](#_ENREF_5) the ubiquitous presence of PAHs in 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](#_ENREF_8) - and via the unidentified infrared (UIR) emission bands probed in the range of 3 to 14 μm.[10](#_ENREF_10), [12-13](#_ENREF_12) The identification of PAHs in carbonaceous chondrites such as Murchison along with 13C/12C isotopic studies convincingly support an interstellar origin.[14](#_ENREF_14) Based on extensive combustion models, it is recommended that the hydrogen abstraction - acetylene addition mechanism (HACA) dictates the synthesis of polycyclic aromatic hydrocarbons (PAHs) not only in sooting combustion flames, but also in circumstellar envelopes of dy­ing Asymptotic Giant Branch (AGB) stars such as IRC+10216.[2](#_ENREF_2), [4](#_ENREF_4), [15-18](#_ENREF_15) Here, the HACA route proposes a recurring sequence via abstraction of a hydrogen atom from the reac­ting aromatic hydrocarbon (arylH) 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 (C2H2) yielding the sty­re­­n­yl radical (C8H7) (Scheme 1). The addition of the second acetylene molecule proceeds either to the sty­re­­n­yl radical or to the ortho-vinylphenyl radical (C8H7), 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 prominent temperatures up to 1,000 K.[3](#_ENREF_3" \o "Frenklach, 1989 #538) However, although naphthalene (C10H8) has been revealed experi­men­tally as an *overall* pro­duct of the reaction of the phenyl radical with two acetylene molecules,[19](#_ENREF_19) the underlying *elemen­tary reactions* of the sty­re­­n­yl and of the ortho-vinylphenyl radicals with acetylene leading to naphthalene have *never* been explored experimentally. Sin­ce combus­tion models are essenti­ally troubled with *likely* reac­tion pathways to PAH syn­thesis, detailed mechanistic studies driving the PAH formation have remained largely speculative, and even the formation me­cha­­nisms of the PAH prototype - the naphthalene mole­cule (C10H8) – 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 of the 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 (Scheme 1). Conducted in a simu­la­ted combustion environ­ment, this study provides the very 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 the simplest PAH – naph­tha­­­lene (C10H8) – 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 (Re-TOF) provide the ultimate evidence in the elucidation of the fundamental, elementary reaction mechanisms forming naph­tha­­­lene within the framework of the HACA mechanism operating at elevated temperature 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 separately. Briefly, the sty­re­­n­yl and the ortho-vinyl­phe­nyl radicals were generated via pyrolysis of beta-bromostyrene and 2-bromostyrene (C8H7Br). These pre­cur­sors were seeded in neat acetylene of 400 Torr, which in turn was expanded into a resistively heated silicon carbide tube (SiC) kept at a temperature of 1,500 ± 50 K (‘che­mi­cal reactor’). The acetylene acted as the seeding and the reactant gas with the pyroly­tically generated radicals. The exceptional benefit of this setup is the capability to 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 (ReTOF) mass spectrometer, 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. Note that 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 the sty­re­­n­yl with acetylene (Figure 1.a) and ortho-vinylphenyl with acetylene (Figure 1.b) spectra; reference spectra obtained by replacing the acetylene reactant with helium carrier gas are also presented in Figures 1.c and 1.d. 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 (*m/z*) of 102 to 104. The ion counts at *m/z* of 104 and 102 originate from C8H8+and C8H6+, respectively. Signal at *m/z* of 103 could account for 13CC7H6+ at levels of up to 10% with respect to C8H6+, along with C8H7+, i.e. the photoionized sty­re­­n­yl and ortho-vinylphenyl radicals. Note that all spectra depict signal at *m/z* of 182 and 184, which stem from the photoionized, non-pyrolyzed C8H779Br and C8H781Br precursors, respectively. These ion counts are common to all helium and acetylene seeded systems and, therefore, do not origin from bimolecular reactions between the sty­re­­n­yl/ortho-vinylphenyl radicals and acetylene. On the other hand, signal at *m/z* = 128 and 126 as well as m/z = 128 are unique to the acetylene-seeded sty­re­­n­yl and ortho-vinylphenyl systems (Figures 1.a and 1.b, respectively). As a consequence, products of the chemical formula C10H8 (128 amu) and C10H6 (126 amu) must resemble *reaction products* between the sty­re­­n­yl/ortho-vinylphenyl radicals and acetylene. More specifically, the C10H8 product (128 amu) is syn­the­sized via the reaction of the C8H7 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, the hydrocarbon isomer(s) of the molecular formula C10H8 is formed in both systems.

(1) C8H7 + C2H2 → C10H8 + H

     However, which isomer is formed? To identify the nature of the product isomer(s), we are switching our focus to the analysis of the photoionization efficiency (PIE) curves, which report the intensities of the ions at *m/z* = 128 (C10H8+) as a function of the photon energy (Figure 2). The experimentally recorded PIE curves can be then compared with known PIE curves from the litera­ture for distinct isomers of C10H8. Here, the experi­men­tal data as displayed in black can be reproduced exceptionally well with the reference PIE curve of naphthalene[20](#_ENREF_20) superimposed in red for both the sty­re­­n­yl with acetylene and ortho-vinylphenyl with acetylene systems. We also investigated reference PIE curves of alternate isomers like azu­lene (C10H8). However, the PIE curve of azulene does not replicate the experimental data; the onset of the reference PIE curve of azulene starts at 7.42 eV, which is about 0.7 eV lower in energy than our experimental data. We would like to highlight that the PIE curve of C10H8 is *uniquely connected* 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 contributor 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 (C6H5CCH; C8H6) (102 amu) and of styrene (C6H5C2H3; C8H8) (104 amu) possibly via hydrogen atom loss and addition to the sty­re­­n­yl (C8H7; 103 amu) and ortho-vinylphenyl (C8H7; 103 amu) ra­di­cals, respectively.[18](#_ENREF_18) The PIEs at *m/z* = 103 could be reproduced with solely 13C-substituted phenyl acetylene (13CC7H6) (103 amu). This finding suggests that once formed, the sty­re­­n­yl and ortho-vinylphenyl radicals (103 amu) do not survive the 18 ± 4 μs residence time within the chemical reactor (Materials & Methods), but rather decompose via atomic hydrogen loss to phenylacetylene or react with acetylene to form eventually naphthalene under our experimental con­ditions.[18](#_ENREF_18) Alex, please add discussion on p, T how is correlates w/ your predictions on the stability of C8H7] The temperature of 1,500 ± 50 K within the ‘chemical reactor’ is high enough to overcome the barrier of XXX kJ mol-1 of the hydrogen shift between the sty­re­­n­yl and ortho-vinylphenyl radicals.[[1]](#endnote-1) The PIE curve at *m/z* = 126 might originate from the diethynylbenzene isomers, in which the only reference PIE curve of 1,4-diethynylbenzne is overlaid well with the experimental curve (Supporting Information).

Our experiments demonstrate convincingly for the very first time that the naphthalene mole­cu­le is synthesized in the pyroly­tic reactor under combustion like conditions via the reaction of the sty­re­­n­yl and ortho-vinylphenyl radicals with acetylene involving the HACA routes as compiled in Scheme 1. Here, the reactions of sty­re­­n­yl/ortho-vinylphenyl are initiated by addition of acetylene via barriers of 20 and 16 kJ mol-1; the collision complexes were found to be bound by 165 and 157 kJ mol-1 with respect to the sepa­rated reactants[18](#_ENREF_18) and undergo ring closure to 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 located 51 and 28 kJ mol-1 above the separated products.[18](#_ENREF_18) [Alex, please check]

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 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. Nevertheless, the unambiguous expression of the HACA pathways along with the detection of the simplest 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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**Materials and Methods**

**Experimental:** Experiments were carried out at the Chemical Dynamics Beamline (9.0.2) of the Advanced Light Source in the Lawrence Berkeley National Laboratory. Employing a resistively-heating high-temperature silicon carbide tube (chemical reactor), the molecular beam apparatus is equipped with a Wiley-McLaren reflectron time-of-flight mass spectrometer (ReTOF). The chemical reactor mimics combustion-relevant conditions such as temperature and pressure along with chemical reactions to synthesize PAHs *in situ* involving reactions of combustion-relevant radicals. Here, sty­re­­n­yl and ortho-vinyl­phenyl radicals (C8H7) were generated *in situ* via pyrolysis of beta-bromostyrene or 2-bromostyrene (C8H7Br; Sigma Aldrich) seeded in neat acetylene or helium gases of 400 Torr in a temperature of 1,500 ± 50 K, respectively. The concentrations of beta/2-bromostyrene in acetylene/helium were estimated to be less than 0.1%, and the residence time of the reactant within the tube was determined to be about 18 ± 4 μs. The temperature of the silicon carbide tube was monitored using a Type-C thermo­couple.

The acetylene gas did not only act as a carrier gas, but also as a reactant with the pyro­ly­tically generated radicals. Reaction products generated in the reactor were expanded supersonically and passed through a 2 mm diameter skimmer located 10 mm downstream and into the main chamber, which houses the Re-TOF. The quasi-continuous tunable vacuum ultraviolet (VUV) light from the Advanced Light Source intercepted the neutral molecular beam in the extraction region of a Wiley–McLaren ReTOF. VUV single photon ionization profits from fragment-free ionization and hence is defined as a soft ionization method in comparison to electron impact ionization, which often results in excessive fragmentation of the parent ion. The ions formed via photo­ioni­zation are then extracted perpendicular to the molecular beam and fed onto a microchannel plate detector by an ion lens. Photoionization efficiency curves, which report ion counts as a function of photon energy, at a particular mass-to-charge ratio (m/z) were extracted by integrating the signal recorded at the specific m/z selected for the species of interest over the energy range 8.000 eV to 11.000 eV in 0.025 eV increments and normalized to the total photon flux. We also conducted blank experiments by expanding only acetylene carrier gas (C2H2) into the resistively-heated silicon carbide (SiC) tube and by replacing acetylene with helium carrier gas. No naphthalene reaction products were observed in these control experiment.

Scheme 1: Schematic representation of the modified Frencklach (red) and Bittner-Hoffmann (blue) reaction sequence leading to the formation of naphthalene via styrenyl and ortho-vinylphenyl radicals, respectively. The reaction sequences in our experiments start with the reaction of styrenyl and ortho-vinylphenyl radicals with acetylene. Note that the temperature of 1,500 ± 50 K within the ‘chemical reactor’ is sufficiently high enough to overcome the barrier of XXX kJmol-1 of the hydrogen shift between the sty­re­­n­yl and ortho-vinylphenyl radicals.[[2]](#endnote-2) Therefore, both radicals coexist at a thermodynamical equilibrium in each experiment.

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