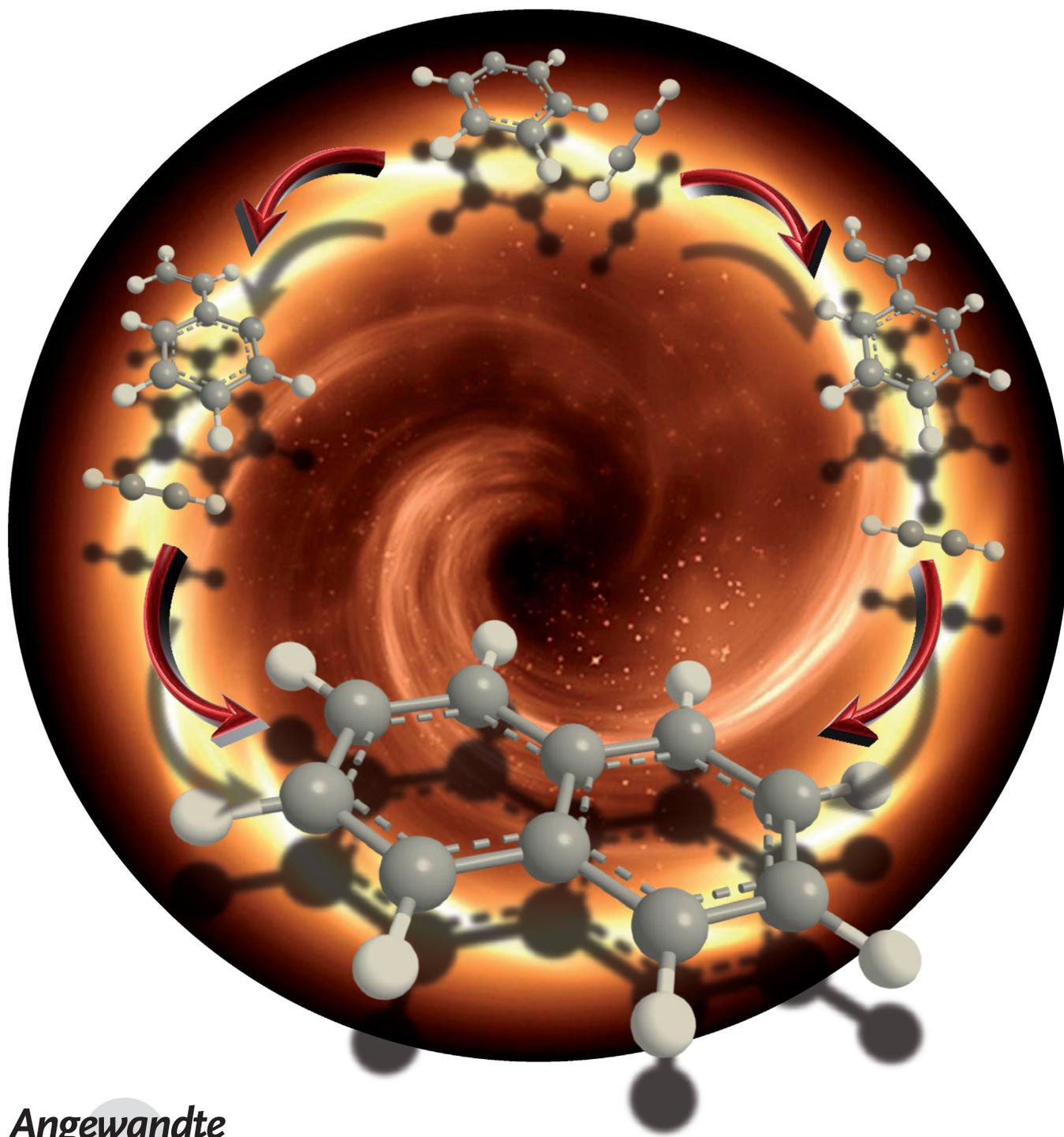


# Hydrogen Abstraction/Acetylene Addition Revealed\*\*

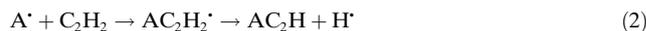
*Dorian S. N. Parker, Ralf I. Kaiser,\* Tyler P. Troy, and Musahid Ahmed\**



**Abstract:** For almost half a century, polycyclic aromatic hydrocarbons (PAHs) have been proposed to play a key role in the astrochemical evolution of the interstellar medium (ISM) and in the chemistry of combustion systems. However, even the most fundamental reaction mechanism assumed to lead to the simplest PAH naphthalene—the hydrogen abstraction–acetylene addition (HACA) mechanism—has eluded experimental observation. Here, by probing the phenylacetylene ( $C_8H_6$ ) intermediate together with naphthalene ( $C_{10}H_8$ ) under combustion-like conditions by photo-ionization mass spectrometry, the very first direct experimental evidence for the validity of the HACA mechanism which so far had only been speculated theoretically is reported.

In recent decades electronic structure calculations and kinetic models proposed the hydrogen abstraction–acetylene addition (HACA) mechanism to dominate the formation of polycyclic aromatic hydrocarbons (PAHs)—organic molecules carrying fused benzene rings—in combustion flames<sup>[1]</sup> and in the interstellar medium (ISM).<sup>[2]</sup> Since the very first postulation of their interstellar relevance as the missing link between small carbon clusters and carbonaceous nanoparticles (interstellar grains), PAHs have been suggested to contribute up to 30% of the interstellar carbon budget and have also been associated with the prebiotic evolution of the interstellar medium.<sup>[3]</sup> Their ubiquitous interstellar presence has been inferred from the diffuse interstellar bands (DIBs)<sup>[4]</sup>—discrete absorption features superimposed on the interstellar extinction curve ranging from the blue part of the visible (400 nm) to the near-infrared (1.2  $\mu$ m)—and through the unidentified infrared (UIR) emission bands observed in the range of 3 to 14  $\mu$ m.<sup>[5]</sup> The detection of PAHs in carbonaceous chondrites strongly advocates an interstellar origin.<sup>[6]</sup>

Being the backbone of PAH formation, the HACA mechanism implies a repetitive reaction sequence of an abstraction of a hydrogen atom from the reacting aromatic hydrocarbon (AH) by a hydrogen atom [reaction (1)] followed by addition of an acetylene molecule ( $C_2H_2$ ) to the radical site [reaction (2)] with A being an aromatic species:<sup>[1a–d]</sup>



Starting from benzene ( $C_6H_6$ ), this mechanism is suggested to lead first to the phenyl radical ( $C_6H_5$ ) followed by addition of an acetylene molecule ( $C_2H_2$ ) forming the styrenyl radical ( $C_8H_7$ ).<sup>[7]</sup> The second step of the HACA mechanism—a subsequent acetylene addition to the *ortho*-vinylphenyl radical ( $C_8H_7$ ) formed by isomerization of the styrenyl species ( $C_8H_7$ )—or hydrogen abstraction from the phenylacetylene molecule ( $C_8H_6$ ) followed by addition of another acetylene molecule ( $C_2H_2$ ) ultimately yields naphthalene ( $C_{10}H_8$ )—the simplest PAH—by cyclization and hydrogen abstraction at elevated temperatures of up to 1000 K.<sup>[1c,d,2,8]</sup> However, despite the popularity of the HACA mechanism, it has not been observed experimentally. Flame models are plagued by an overwhelming number of possible reaction pathways, and it is complicated to truly ascertain from which reactants distinct PAHs are formed. Therefore, mechanistic routes to PAH synthesis have remained conjectural, and the formation mechanisms of even the simplest PAH representative—the naphthalene molecule ( $C_{10}H_8$ )—by the HACA mechanism has not been experimentally corroborated.

Here, in a simulated combustion environment we provide compelling experimental evidence for the formation of naphthalene ( $C_{10}H_8$ ) by the reaction of the phenyl radical ( $C_6H_5$ ) with two acetylene ( $C_2H_2$ ) molecules in a direct observation of the HACA mechanism. By exploiting the unique advantage of fragment-free photoionization by tunable vacuum ultraviolet (VUV) light and detection of the ionized molecules via a reflectron time of flight mass spectrometer (ReTOF), we are able to identify the isomer specific reaction products of the HACA mechanism and rationalize the reaction mechanism.

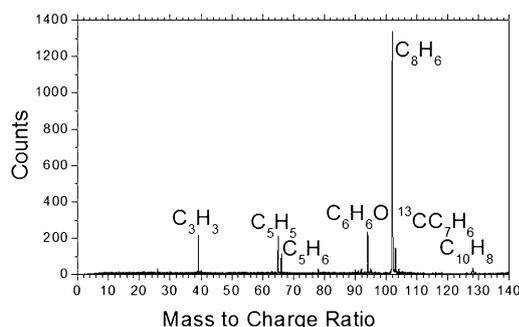
The prototype PAH naphthalene ( $C_{10}H_8$ ) and the HACA mechanism byproduct phenylacetylene ( $C_8H_5CCH$ ) were formed by a directed synthesis through reaction of the phenyl radical ( $C_6H_5$ ) with two acetylene molecules ( $C_2H_2$ ; Experimental Section). Here, a continuous beam of phenyl radicals ( $C_6H_5$ ) was generated in situ by a quantitative pyrolysis of nitrosobenzene ( $C_6H_5NO$ ). The latter was seeded in neat acetylene ( $C_2H_2$ ), which was expanded at a pressure of 300 Torr into a resistively heated silicon carbide tube at a temperature of  $1020 \pm 100$  K (“chemical reactor”). The acetylene molecules did not only act as a seeding gas, but also as a reactant with the pyrolytically generated phenyl radicals. The neutral molecular beam were interrogated by quasi continuous tunable vacuum ultraviolet (VUV) radiation in the extraction region of a ReTOF mass spectrometer. The photoionized molecules were then collected by a micro-channel plate (MCP) detector. A mass spectrum was obtained at intervals of 0.025 eV between 8.0 and 11.0 eV.

Figure 1 depicts the mass spectrum recorded at 9 eV photoionization energy with product peaks at the relevant mass-to-charge ratios of  $m/z = 102$  ( $C_8H_6^+$ ) and  $m/z = 128$  ( $C_{10}H_8^+$ ). Considering the molecular mass of the reactants and of the neutral products, we can see that the  $C_8H_6$  and  $C_{10}H_8$  products are formed by reaction of the phenyl radical ( $C_6H_5$ ;

[\*] Dr. D. S. N. Parker, Prof. R. I. Kaiser  
 Department of Chemistry, University of Hawaii at Manoa  
 Honolulu, HI 96822, (USA)  
 E-mail: ralfk@hawaii.edu  
 Homepage: <http://www.chem.hawaii.edu/Bil301/welcome.html>  
 Dr. T. P. Troy, Dr. M. Ahmed  
 Chemical Sciences Division  
 Lawrence Berkeley National Laboratory  
 Berkeley, CA 947200 (USA)

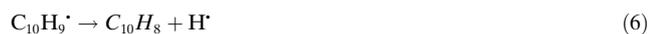
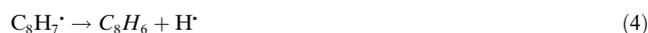
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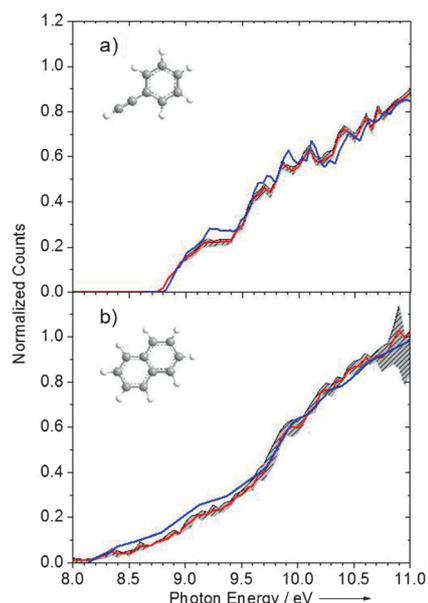


**Figure 1.** Mass spectrum of the products of the reaction of phenyl radicals with acetylene in the chemical reactor recorded at a photon energy of 9.0 eV.

77 u) with one acetylene ( $C_2H_2$ ; 26 u) and two acetylene molecules, respectively [reactions (3)–(6)] with the detected reaction products stated in italics.



The interpretation of the raw data provides convincing evidence that in the reaction of phenyl radicals with acetylene, hydrocarbons of the molecular formula  $C_8H_6$  and  $C_{10}H_8$  are formed. We shift our attention now to the identification of the product isomer(s) formed based on an analysis of the photoionization efficiency (PIE) curves, which report the intensities of the ions at  $m/z = 102$  ( $C_8H_6^+$ ) and  $m/z = 128$  ( $C_{10}H_8^+$ ) as a function of photon energy (Figure 2). The experimental data as displayed in black matches well reference photoionization efficiency curves of phenylacetylene ( $C_8H_6$ )<sup>[9]</sup> and naphthalene ( $C_{10}H_8$ ) isomers<sup>[10]</sup> overlaid in blue. Therefore, we can conclude that peaks at  $m/z = 102$  and 128 originate solely from the phenylacetylene ( $C_6H_5CCH$ ) and naphthalene ( $C_{10}H_8$ ) isomers, respectively. For completeness, we also checked reference PIE curves of alternative isomers such as azulene ( $C_{10}H_8$ ). However, the PIE curve of azulene cannot reproduce the experimental data since the onset of the PIE arises at 7.42 eV, which is 0.72 eV lower in energy than that seen in our data. Note that the PIE curve at  $m/z = 103$  can be attributed to the presence of  $^{13}C$ -substituted phenylacetylene. It should be stressed that PIE curves of  $C_8H_6$  and  $C_{10}H_8$  isomers are unique to each molecule implying that the presence of other isomers in the molecular beam would alter the shape of the PIEs significantly. Therefore, we conclude that phenylacetylene and naphthalene are solely responsible for the products at  $m/z$  102 and 128, respectively. Using the photoionization cross-sections<sup>[11]</sup> and scaling for photon flux, a naphthalene ( $C_{10}H_8$ ) yield of  $5 \pm 1\%$  compared to phenylacetylene ( $C_8H_6$ ;  $95 \pm 1\%$ ) is determined. Additional signals can be seen at lower masses and have been identified by matching their PIE curves to reference PIEs (see the Supporting Information). The signal at  $m/z = 94$  corre-



**Figure 2.** Photoionization efficiency curves (PIE) recorded at  $m/z = 102$  and 128 shown as red lines along with experimental errors defined as the hatched grey area. The blue lines show the PIE curves for determined experimentally for a) phenylacetylene<sup>[9]</sup> and theoretically for b) naphthalene.<sup>[10]</sup>

sponds to phenol ( $C_6H_6O$ ) arising from the reaction of the phenyl radical with traces of oxygen, which produces the phenoxy ( $C_6H_5O$ ) radical followed by hydrogen abstraction. The small signal at  $m/z = 78$  is attributed to benzene and fulvene likely formed through hydrogen atom addition (and successive isomerization) to the phenyl radical. The resonantly stabilized free radicals (RSFRs) propargyl ( $m/z = 39$ ,  $C_3H_3$ ) and cyclopentadienyl ( $m/z = 65$ ,  $C_5H_5$ ) as well as cyclopentadiene ( $m/z = 66$ ,  $C_5H_6$ ) were observed also. These three species were not seen in either pure acetylene ( $C_2H_2$ ) or nitrosobenzene ( $C_6H_5NO$ ) spectra. We would like to discuss briefly the origin of the product at lower masses. Recent computational investigations suggest that cyclopentadienyl radicals ( $C_5H_5$ ) might be formed through sequential hydrogen atom additions to naphthalene<sup>[12]</sup> or as a result of phenol degradation by hydrogen atom loss to the phenoxy radical followed by carbon monoxide emission (CO) yielding the cyclopentadienyl radical.<sup>[13]</sup> The cyclopentadiene ( $C_5H_6$ ) and benzene molecules ( $C_6H_6$ ) can be formed through hydrogen atom addition to their aromatic radicals, cyclopentadienyl and phenyl, respectively. Once cyclopentadienyl radicals are formed they are expected to further decompose to the propargyl radical and acetylene as demonstrated in shock tube studies<sup>[14]</sup> and theoretical investigations.<sup>[15]</sup> The temperature of  $1020 \pm 100$  K within the chemical reactor is high enough to overcome the reaction barriers to cyclopentadienyl and propargyl formation.

The experiments provide compelling evidence that the naphthalene molecule together with phenylacetylene can be formed in the pyrolytic reactor under combustion-like conditions from its phenyl radical and acetylene precursors by the HACA pathway. The detection of naphthalene together with

phenylacetylene successfully demonstrate reaction pathways corresponding to the HACA mechanism as proposed by Frenklach<sup>[1a-d]</sup> and through the Bittner–Howard<sup>[1e]</sup> route. Here, the phenyl radical ( $C_6H_5$ ) reacts with acetylene to form phenylacetylene through an acetylene versus hydrogen atom exchange pathway. This finding correlates with a study under single collision conditions using crossed molecular beams of phenyl radicals and acetylene, which identified phenylacetylene as the reaction product formed by atomic hydrogen emission.<sup>[16]</sup> Here, phenylacetylene is formed through the barrier-less addition of the phenyl radical to the  $\pi$ -electron density of the carbon–carbon triple bond of acetylene yielding a  $C_8H_7$  reaction intermediate. The  $C_8H_7$  intermediate eventually decomposes by atomic hydrogen emission to phenylacetylene. In contrast to crossed molecular beams experiments, which are conducted under single collision conditions, collisional stabilization is possible in our chemical reactor.

Of the three HACA routes, two can proceed by addition of the second acetylene molecule to the  $C_8H_7$  intermediate. Firstly, the Bittner–Howard pathway is initiated through addition of the phenyl radical to the acetylene molecule to yield the collision complex  $C_8H_7$ ; an addition of a second acetylene molecule onto the acetyl chain forms a  $C_{10}H_9$  intermediate. The C4 chain with the radical located on the terminal carbon cyclizes via radical addition to the phenyl ring and subsequent hydrogen elimination yields naphthalene. Secondly, Frenklach's route<sup>[1a]</sup> involves shifting the radical center of the  $C_8H_7$  intermediate to the phenyl ring by hydrogen migration.<sup>[17]</sup> A second acetylene addition to the  $C_8H_7$  aromatic radical intermediate forms a di-substituted  $C_{10}H_9$  intermediate; cyclization and hydrogen atom emission leads to naphthalene. The third route, and original HACA mechanism proposed by Frenklach involves first the formation of phenylacetylene, followed by hydrogen abstraction from the phenyl ring to form a  $C_8H_5$  intermediate.<sup>[1b-d]</sup> A subsequent addition of acetylene to the ring forms a di-substituted  $C_{10}H_7$  intermediate, cyclization of the radical acetyl group forms a naphthyl radical ( $C_{10}H_7$ ) to which atomic hydrogen can be added to reach naphthalene. Based on the calculated rate constants and barrier heights there is no preferential route discernible between the three routes.<sup>[7]</sup> However, in our experiment we can rule the last reaction route out since we do not see any evidence for a second hydrogen abstraction from phenylacetylene. If the reaction proceeded with a second hydrogen atom abstraction, we would observe products from acetylene addition to the meta and para positions of the aromatic ring which would not cyclize to naphthalene, and therefore change the PIE curves. Additions to the meta and para positions would also likely result in a spread of products with different mass-to-charge ratios such as  $C_{10}H_6$  ( $m/z=126$ ) and  $C_{10}H_{10}$  ( $m/z=130$ ), which are not detected. Considering that we only observe the formation of naphthalene ( $m/z=128$ ) we can rationalize the reaction mechanism proceeds through a second acetylene addition to a  $C_8H_7$  radical intermediate, either by the Frenklach or Bittner–Howard routes.

The facile route to naphthalene ( $C_{10}H_8$ ) formation through the reaction of the phenyl radical ( $C_6H_5$ ) with two

acetylene molecules ( $C_2H_2$ ) together with the detection of phenylacetylene ( $C_6H_5CCH$ ) provides for the first time compelling evidence for the validity of the HACA mechanism under combustion-like conditions. Phenylacetylene and naphthalene represent the first and second products in the HACA-based mass growth process. This mechanism leads to aromatization and PAH formation from a single, monocyclic aromatic species like benzene ( $C_6H_6$ ) or the phenyl radical ( $C_6H_5$ ) at elevated temperatures as present in the combustion processes of fossil fuels and also in circumstellar shells of dying carbon stars close to their photospheres. This repetitive addition of an aromatic radical to acetylene leading ultimately to more complex aromatic hydrocarbon rings might be expanded from naphthalene to build up even tricyclic PAHs such as anthracene and phenanthrene thus holding crucial implications to mass growth processes in circumstellar envelopes, where elevated temperatures of typically 1000 K, and abundant reservoirs of acetylene exist. By replacing the phenyl radical ( $C_6H_5$ ) with the isoelectronic pyridynyl radical ( $C_5H_4N$ ), the HACA route could even open up a hitherto overlooked pathway to quinoline ( $C_9H_7N$ ) formation—the prototype of a nitrogen-substituted PAH—upon reaction with two acetylene molecules thus expanding the crucial significance of the HACA mechanism to combustion sciences and astrochemistry to the more exotic realm of astrobiology and of our origins.

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