

Unexpected Chemistry from the Reaction of Naphthyl and Acetylene at Combustion-Like Temperatures**

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Abstract: The hydrogen abstraction/acetylene addition (HACA) mechanism has long been viewed as a key route to aromatic ring growth of polycyclic aromatic hydrocarbons (PAHs) in combustion systems. However, doubt has been drawn on the ubiquity of the mechanism by recent electronic structure calculations which predict that the HACA mechanism starting from the naphthyl radical preferentially forms acenaphthylene, thereby blocking cyclization to a third six-membered ring. Here, by probing the products formed in the reaction of 1- and 2-naphthyl radicals in excess acetylene under combustion-like conditions with the help of photoionization mass spectrometry, we provide experimental evidence that this reaction produces 1- and 2-ethynynaphthalenes ($C_{12}H_8$), acenaphthylene ($C_{12}H_8$) and diethynynaphthalenes ($C_{14}H_8$). Importantly, neither phenanthrene nor anthracene ($C_{14}H_{10}$) was found, which indicates that the HACA mechanism does not lead to cyclization of the third aromatic ring as expected but rather undergoes ethynyl substitution reactions instead.

The gas-phase reactions of unsaturated hydrocarbons and their radicals rapidly, exothermically, and sequentially form hexagonal six-carbon ring structures leading to large polycyclic aromatic hydrocarbons (PAH) in sooting flames^[1] of, for example, methane,^[2] benzene,^[3] and toluene.^[4] PAHs and their derivatives are considered to be toxic byproducts produced during the incomplete combustion of fossil fuels; these compounds are also linked to food poisoning, cancer,^[5] and global warming.^[6] An intimate understanding of their formation and growth mechanisms is therefore crucial to eventually eliminate the formation of PAHs in combustion processes.

The hydrogen abstraction/acetylene addition (HACA) mechanism has been proposed as a key route to PAH formation in high-temperature environments up to 2500 K.^[1,7] This fundamental route involves the sequential reaction of an aromatic radical such as the phenyl radical ($C_6H_5^\bullet$) with two acetylene (C_2H_2) molecules leading eventually to the simplest PAH, naphthalene ($C_{10}H_8$; Equations (1)–(3)).^[1,8] After formation of naphthalene ($C_{10}H_8$), the HACA mechanism has been proposed to continue through hydrogen atom abstraction from the naphthalene ring leading to the 1- and/or 2-naphthyl radical ($C_{10}H_7^\bullet$),^[9] upon which a third six-membered aromatic ring is proposed to be formed through successive reactions with two acetylene molecules leading to anthracene and phenanthrene ($C_{14}H_{10}$). Reaction of 1-naphthyl radicals with a single acetylene molecule has been proposed to synthesize acenaphthylene ($C_{12}H_8$)—a prospective precursor to nonplanar PAHs like corannulene and possibly to fullerene (Scheme 1).^[10]

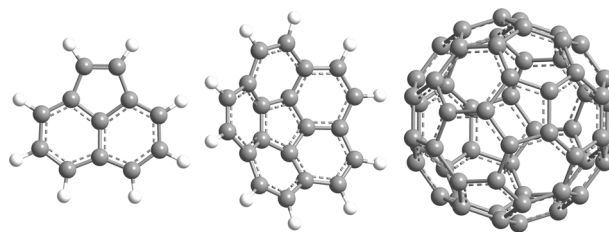


However, recently, the molecular growth processes from naphthalene to anthracene and phenanthrene involving the HACA mechanism have come under scrutiny. Comprehensive electronic structure calculations demonstrate that upon formation of the 1-naphthyl radical ($C_{10}H_7^\bullet$), addition of acetylene (C_2H_2) would form predominantly acenaphthylene ($C_{12}H_8$).^[8a] Mebel et al. provide compelling evidence that the rapid cyclization of the $C_{12}H_9$ intermediate to form a five-membered ring is much faster than the addition of a second acetylene molecule leading to $C_{14}H_{11}$ followed by hydrogen loss to yield a third aromatic ring: anthracene and/or phenanthrene. A comparison of these predictions with data from combustion flames shows that the HACA-type mechanism only accounts for up to 6% of phenanthrene and

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Scheme 1. Structures of acenaphthylene, corannulene, and fullerene.

anthracene at combustion-relevant temperatures from 1000 to 2000 K.^[11] Doubts were raised earlier still on the ability of the HACA mechanism to reach the large mass of high-order PAHs such as coronene (300 u) at the experimentally observed rates, by only adding 24 u in each step.^[12] Although certainly present in combustion environments, HACA routes have often been labeled as the most important routes to PAH formation, simply based on the observation of abundant acetylene, the knowledge that aromatic radicals play a pivotal role in PAH formation, and the neatness of the empirical formula by addition of C_2H_2 followed by hydrogen emission. Recent work by Shukla et al. has shown that phenyl addition cyclization (PAC) forms large-mass PAHs at a much more convincing rate than the HACA mechanism, by addition of 77 u at each step.^[13] Our investigation aims to identify the product distribution for the HACA mechanism leading from the prototypical bicyclic radical, the 1- and 2-naphthyl radicals to tricyclic PAHs phenanthrene and anthracene by sequential addition to acetylene molecules. Although the HACA mechanism operates over a range of aromatic radicals and experimental conditions, our experiment investigates a central pathway from bi- to tricyclic PAHs that is representative of the sequential two-step acetylene addition mechanism that builds an extra aromatic ring onto a PAH radical.

By studying the reactions of the 1- and 2-naphthyl radicals ($C_{10}H_7^{\cdot}$) with acetylene (C_2H_2) under simulated combustion conditions, we provide experimental evidence that the HACA mechanism forms firstly 1- and 2-ethynylnaphthalene ($C_{12}H_8$) and acenaphthylene ($C_{12}H_8$) and secondly diethynyl naphthalenes ($C_{14}H_8$) with surprisingly no formation of the previously postulated tricyclic PAHs phenanthrene and anthracene ($C_{14}H_{10}$). The isomer-specific products of these reactions were monitored and identified by exploiting single-photon ionization by tunable vacuum ultraviolet (VUV) light.^[14] Ionized molecules were detected by reflectron time-of-flight mass spectrometry (ReTOF). In separate experiments, continuous beams of 1-naphthyl and 2-naphthyl radicals ($C_{10}H_7^{\cdot}$) were generated in situ through quantitative pyrolysis of their 1- and 2-iodonaphthalene ($C_{10}H_7I$) precursors, respectively. Each precursor was seeded in pure acetylene (C_2H_2) at pressures of 300 Torr and expanded into a resistively heated silicon carbide tube ("pyrolytic reactor") at 1200 ± 100 K.^[15] The acetylene molecules did not only act as a seeding gas, but also as a reactant with the pyrolytically generated naphthyl radicals. The neutral molecular beam was then interrogated by quasicontinuous tunable vacuum ultraviolet (VUV) radiation in the extraction region of a ReTOF mass spectrometer. The photoionized molecules were collected by a microchannel plate detector with mass spectra being collected at intervals of 0.05 eV between 8.00 and 10.00 eV (see the Supporting Information, SI).

Figure 1 depicts the mass spectra for the reaction of 1-naphthyl and 2-naphthyl radicals with acetylene recorded at a photoionization energy of 9.0 eV. These data provide clear evidence for the presence of products at m/z 152 ($C_{12}H_8^+$) and m/z 176 ($C_{14}H_8^+$). It is important to highlight the absence of any products at m/z 178 ($C_{14}H_{10}^+$). Considering the molecular masses of the reactants and products, the $C_{12}H_8$ (152 u) and

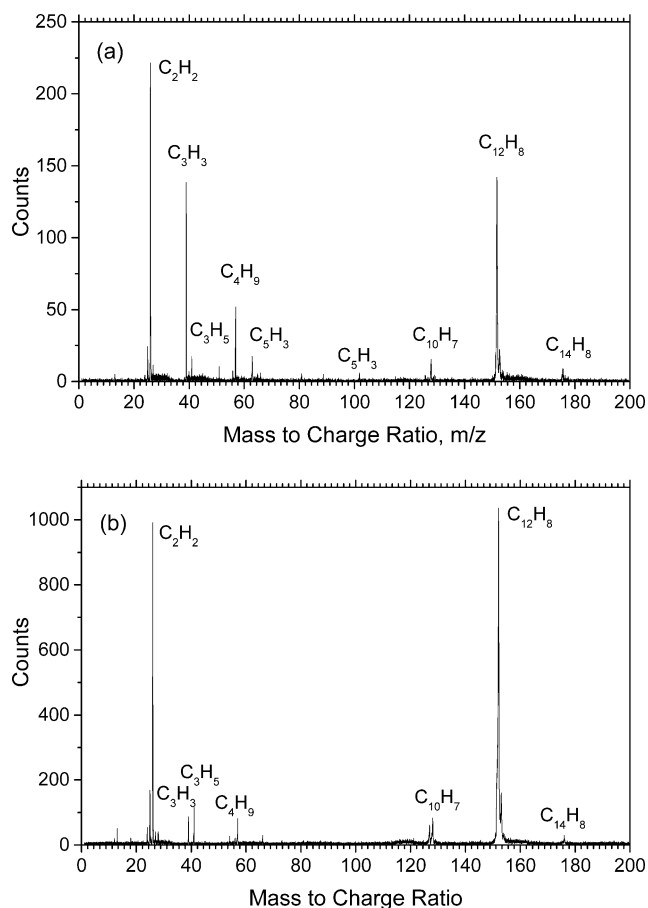


Figure 1. Mass spectra of the products of the reaction of a) 1-naphthyl and b) 2-naphthyl radicals with acetylene in the pyrolysis reactor at a pressure of 300 Torr recorded at a photon energy of 9.0 eV.

$C_{14}H_8$ (176 u) products are formed through the reaction of the naphthyl radical ($C_{10}H_7^{\cdot}$; 127 u) with one and two acetylene molecules (C_2H_2 ; 26 u) through a series of acetylene addition/hydrogen atom eliminations [Equations (1)–(3)] with the molecules indicated in bold detected in the present study. The interpretation of the mass spectra alone provides clear proof that in the reaction of naphthyl radicals with acetylene, only the hydrocarbons of the molecular formulae $C_{12}H_8$ and $C_{14}H_8$ are formed and no $C_{14}H_{10}$ isomers. Therefore, we conclude that neither phenanthrene nor anthracene are reaction products under the present experimental conditions. It should be noted that both, phenanthrene and anthracene, have been observed and studied under identical conditions in the experimental apparatus in which they are fully observable and identifiable. Furthermore, in the preparation stages of the experiment, the reactions were conducted at a range of temperatures while monitoring the mass spectra for the signal at m/z 178 ($C_{14}H_{10}$); no signal was observed at any temperature from no heating to 1500 K.

We now focus on the identification of each isomer by analyzing the photoionization efficiency (PIE) curves, which report the intensity of the $C_{12}H_8^+$ and $C_{14}H_8^+$ ions as a function of photon energy (Figure 2). These data are compared with known reference curves for $C_{12}H_8$ and $C_{14}H_8$ isomers.^[16] The experimental PIE curves are displayed in black along with the

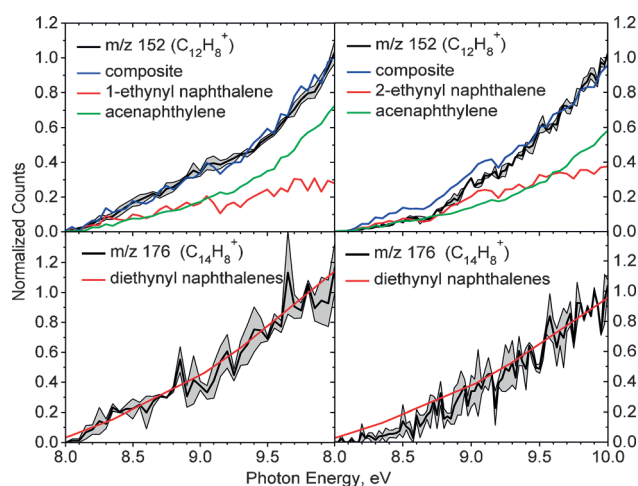


Figure 2. Photoionization efficiency curves recorded at m/z 152 ($C_{12}H_8^+$) and m/z 176 ($C_{14}H_8^+$) for the reaction of 1-naphthyl (left column) and 2-naphthyl (right column) with acetylene. The black line represents the experimental data with the error limits defined as shaded areas. Colored lines represent the fits (see text for details).

error limits defined as the shaded areas. The photoionization efficiency curves of m/z 152 ($C_{12}H_8^+$; Figure 2a and c) can be reproduced nicely by a linear combination of the reference PIE curves of 1- and 2-ethynyl naphthalene ($C_{12}H_8$; red) and acenaphthylene ($C_{12}H_8$; green) with branching ratios of typically 2.0:(3.0 \pm 0.5), that is, a slight preference of acenaphthylene formation. The PIEs for m/z 176 ($C_{14}H_8^+$; Figure 2b and d) can be fit within our error limits through a linear combination of diethynyl naphthalene isomers 1,5- and 1,8-diethynyl naphthalene.^[16–17] Accounting for the photoionization cross sections and scaling for photon fluxes,^[15a] the ratio of products at m/z 152 and m/z 176 are derived to be 95 \pm 1% and 5 \pm 1%, respectively. Considering the lack of any signal at m/z 178 ($C_{14}H_{10}^+$), we can firmly conclude that no tricyclic PAHs (anthracene, phenanthrene) are formed under our experimental conditions. It should be noted that the reaction of phenyl radicals with acetylene was investigated using the same apparatus and pressure, and temperature of 1020 K.^[8b] Here, phenylacetylene and naphthalene were observed as the first and second products of the HACA mechanism, in the ratio of 95 \pm 1% and 5 \pm 1%, respectively, showing that experimental conditions are conducive to cyclization if mechanistically possible.^[8b]

From the failed observation of anthracene and phenanthrene, but the simultaneous formation of diethynyl naphthalenes ($C_{14}H_8$; 176 u) as well as acenaphthylene ($C_{12}H_8$; 152 u), we can extract crucial information on the molecular growth processes (or the lack thereof) leading to PAHs beyond the second six-membered aromatic ring. First, the experimental results can be rationalized if a single acetylene molecule reacts with the 1- and 2-naphthyl radicals forming a $C_{12}H_9$ intermediate [Eq. (1)], which then loses a hydrogen atom to form 1- and 2-ethynyl naphthalene ($C_{12}H_8$) or undergoes ring-closure prior to hydrogen atom loss yielding acenaphthylene ($C_{12}H_8$). Second, as predicted by Mebel et al.,^[8a,11] we have verified that under our experimental conditions, this hydro-

gen atom loss is much faster than the consecutive addition of an acetylene molecule to the $C_{12}H_9$ intermediate yielding $C_{14}H_{11}$, which would be required to form anthracene and/or phenanthrene. Therefore, based on our experimental data, we can conclude that the HACA-type reaction sequence is very limited in forming anthracene and/or phenanthrene and forms ethynyl-substituted molecules instead. Note that the reaction of 2-naphthyl with acetylene should not form acenaphthylene; however, the detection of acenaphthylene implies a fast hydrogen transfer process and/or hydrogen-atom-assisted isomerization from 2-naphthyl to 1-naphthyl, barriers which could be as low as 20 kJ mol^{−1}.^[18] Third, a hydrogen abstraction from ethynyl naphthalene ($C_{12}H_8$) forming the $C_{12}H_7$ radical followed by acetylene addition and consecutive hydrogen atom loss to form diethynyl naphthalene ($C_{14}H_8$) [Equations (2) and (3)] is required to reconcile the experimental data. To verify this conclusion, we repeated the experiments at a reduced pressure of only 50 Torr with the premise that a reduction in pressure should lower the yield of disubstituted naphthalene products due to the reduced collision frequency of the radical intermediates with the acetylene reactants (SI). As a matter of fact, only products at m/z 152 ($C_{12}H_8^+$), which correspond to 1-ethynyl naphthalene and 2-ethynyl naphthalene, for the 1-naphthyl and 2-naphthyl reactions, respectively, were formed; no products were observed at m/z 176 and/or m/z 178. Finally, in both reactions, signal at lower masses— m/z 102 ($C_8H_6^+$), 63 ($C_5H_3^+$), 57 ($C_4H_9^+$), 39 ($C_3H_3^+$), and 26 ($C_2H_2^+$)—can be attributed to the thermal fragmentation of products and intermediates (SI). Based on these masses alone, none of these lower-order fragments contribute to product formation.^[8b]

In summary, the present study provides compelling evidence that the HACA mechanism—under the present experimental conditions of 300 Torr and 1200 K—is unable to form appreciable tricyclic PAHs from the bicyclic radical reactant whilst still undergoing secondary acetylene addition. These findings are in direct contrast to previous experiments showing unitary cyclization to naphthalene upon the reaction of phenyl radicals with excess acetylene.^[8b] The formation of acenaphthylene closes the prospect of the secondary acetylene addition to cyclize to a PAH as previously shown theoretically.^[8a] The increase from mono- to bicyclic aromatic radicals has also increased the number of ring hydrogens that can be abstracted but not undergo cyclization. The result upon addition of a second acetylene is a diethynyl-substituted aromatic instead of aromatic ring formation. The absence of tricyclic PAHs anthracene and phenanthrene ($C_{14}H_{10}$) is potentially representative of the inability of the HACA mechanism to be an effective route to ring formation for PAH formation beyond naphthalene. These findings build on a growing body of experimental evidence suggesting the HACA mechanism is not the most significant mechanism in mass growth to high-mass PAHs opening the door to other competing mechanisms such as PAC^[13] or vinylacetylene addition to aromatic radicals.^[19]

Keywords: combustion · gas-phase chemistry · mass spectrometry · polycyclic aromatic hydrocarbons · radicals

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