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Selective Formation of Indene through the Reaction of Benzyl Radicals with Acetylene

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The combustion of fossil fuels forms polycyclic aromatic hydrocarbons (PAHs) composed of five- and six- membered aromatic rings, such as indene (C_9H_8), which are carcinogenic, mutagenic, and deleterious to the environment. Indene, the simplest PAH with single five- and six-membered rings, has been predicted theoretically to be formed through the reaction of benzyl radicals with acetylene. Benzyl radicals are found in significant concentrations in combustion flames, owing to their highly stable aromatic and resonantly stabilized free-radical character. We provide compelling experimental evidence that indene is synthesized through the reaction of the benzyl radical (C_7H_7) with acetylene (C_2H_2) under combustion-like conditions at 600 K. The mechanism involves an initial addition step followed by cyclization and aromatization through atomic hydrogen loss. This reaction was found to form the indene isomer exclusively, which, in conjunction with the high concentrations of benzyl and acetylene in combustion environments, indicates that this pathway is the predominant route to synthesize the prototypical five- and six-membered PAH.

Since the accidental discovery of the triphenyl radical by Gomberg in 1900,[1] the role of aromatic and resonantly stabilized free radicals in organic chemistry has fascinated scientists. The benzyl radical (C_7H_7) possesses these same properties and has received considerable attention, owing to its abundance in combustion environments. These types of transient species undergo a series of fast radical-mediated reactions that result in the formation of polycyclic aromatic hydrocarbons (PAHs) and ultimately lead to soot particle nucleation through successive mass-growth processes. Here, PAHs containing both five- and six-membered aromatic rings, such as benzo[a]pyrene, are acutely carcinogenic and mutagenic,[2] and are further responsible for global warming.[2a] Therefore, the formation mechanism of PAHs and related derivatives such as (de)hydrogenated and substituted PAHs must be understood and mitigated. The indene molecule (C_9H_8) represents the simplest PAH, containing both a five- and six-membered ring, and has been found in high concentrations in combustion flames such as ethane,[3] propene,[4] *n*-butane,[5] butadiene,[6] toluene,[7] and benzene.[8] This molecule also represents the simplest building block of nonplanar PAHs like corannulene.

However, despite the importance of indene as a prototypical PAH carrying six- and five-membered rings,[9] the formation mechanisms leading to indene have remained speculative to date. A key contending route was predicted by Bittner and Howard through the reaction of the benzyl radical (C_7H_7) with acetylene (C_2H_2) via a hydrogen-abstraction/acetylene-addition (HACA)-type mechanism.[10] The rationale of this proposed route was based on analytical evidence of benzyl radicals (C_7H_7) detected in significant concentrations in combustion flames, owing to their high thermodynamic stability derived from the possession of both aromatic and resonantly stabilized free-radical characteristics. The bond dissociation energy of benzyl hydrogen atoms is 377 kJ mol^{-1} compared to the ring hydrogens of 473 kJ mol^{-1} in toluene,[11] implying that the initial products of toluene pyrolysis are benzyl radicals and atomic hydrogen.[12] Furthermore, theoretical calculations show low entrance barriers and exothermicity in the reaction of benzyl radicals (C_7H_7) with acetylene (C_2H_2) to form indene through hydrogen emission.[13] Recent high-level calculations confirm that the reaction has to overcome a barrier of 50–65 kJ mol^{-1}, which is surmountable under combustion conditions.[14] Alternative reactions involving phenyl radicals (C_6H_5) with allene and its methylacetylene isomer (C_3H_4) lead to indene formation, but only with branching ratios of 70 and 10%, respectively.[15]

Here, we show that the reaction of the benzyl radical (C_7H_7) with acetylene (C_2H_2) under simulated combustion conditions forms the simplest prototypical PAH, indene (C_9H_8), carrying a six- and a five-membered ring, through a bimolecular gas-phase reaction. Our investigation further aims to elucidate the branching ratio between indene and alternative non-PAH isomers that are potentially formed in this reaction. Here, the reaction of the benzyl radical (C_7H_7) with acetylene (C_2H_2) was examined under combustion-relevant conditions, exploiting a resistively heated high-temperature pyrolytic reactor incorporated into a molecular-beam chamber equipped with a Wiley–McLaren Reflectron time-of-flight mass spectrometer (Re-TOF)[16] at the Advanced Light Source (ALS) at the Chemical Dynamics Beamline. Briefly, a continuous beam of benzyl radicals (C_7H_7) was generated in situ through the pyrolysis of benzyl bromide (C_7H_7Br) via carbon–bromine bond cleavage and at concentrations of less than 0.1%. Based on the intensity of the benzyl bromide without and with heating of the silicon carbide tube, conversions of 90 ± 5% were obtained. Benzyl bromide was seeded in neat acetylene (C_2H_2) that was expanded at a pressure of 300 Torr into a resistively heated silicon carbide tube at a temperature of 600 ± 100 K (pyrolytic reactor); note that acetylene not only acts as a seeding gas, but is also a reac-

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tant. Upon exiting the silicon carbide tube and passing through a skimmer, neutral molecules within the supersonic beam were photoionized by single-photon ionization utilizing quasi-continuous tunable vacuum ultraviolet (VUV) radiation. A mass spectrum was obtained at intervals of 0.05 eV between 8.00 and 11.00 eV up to 254 amu. Photoionization efficiency curves (PIEs), which report the ion counts at a particular mass-to-charge (m/z) ratio as a function of photon energy, were obtained by integrating the signal at a well-defined m/z ratio selected for the species of interest over the energy range and normalizing to the total photon flux.

Figure 1 depicts a typical mass spectrum recorded at a photoionization energy of 9.5 eV with prominent product peaks at $m/z=92$ ($C_7H_8^+$) and 116 ($C_9H_8^+$). If we consider the mass of the benzyl radical reactant of 91 amu, we rationalize that the product peak at $m/z=92$ is formed through hydrogen-atom abstraction by the radical to form a C_7H_8 isomer; also, this mass can have contributions from the ^{13}C-substituted benzyl radical (92 amu; $^{13}CC_6H_8^+$). The second product peak at $m/z=116$ is rationalized to originate from the addition of the benzyl radical to the secondary reactant acetylene, which has a mass of 26 amu, followed by hydrogen atom (1 amu) emission to form C_9H_8 isomer(s). Therefore, the analysis of the raw data (mass spectra) alone provides convincing evidence that products of the molecular formulae C_7H_8 and C_9H_8 are formed in the reaction of benzyl radicals with acetylene.

To determine the isomers of the products at $m/z=92$ (C_7H_8) and 116 (C_9H_8), we analyze the PIE curve for $C_7H_8^+$ and $C_9H_8^+$. Figure 2 and Figure 3 report the PIEs for ions collected at $m/z=92$ ($C_7H_8^+$) and 116 ($C_9H_8^+$), shown as black lines along with error boundaries depicted as a shaded area, which were determined by the spread of three identical scans. Figure 2 is fitted by a linear combination (red line) of contributions from the ^{13}C-substituted benzyl radical ($^{13}CC_6H_8^+$; blue line), as recorded at $m/z=91$ (99%) and a smaller contribution from the experimental reference PIE for toluene (C_7H_8; green line) (1%).[17] The PIE curve for the signal at $m/z=116$ was fitted exclusively to the

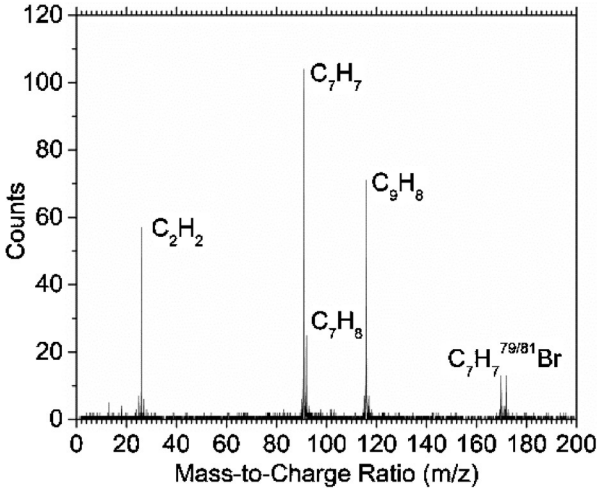

Figure 1. Representative mass spectrum recorded at a photon energy of 9.50 eV in the reaction of benzyl radicals with acetylene. Peaks at $m/z=170$ and 172 are connected with the benzyl radical precursor, benzyl bromide ($C_7H_7^{79}Br$, 170 amu/$C_7H_7^{81}Br$, 172 amu).

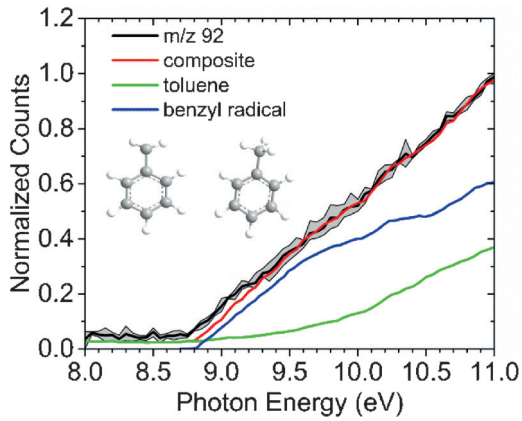

Figure 2. PIE curve recorded at $m/z=92$ shown as a black line, with experimental errors defined as a shaded area. The experimentally determined PIE curve for the benzyl radical is shown as the blue line, toluene as the green line, along with their composite PIE as the red line.

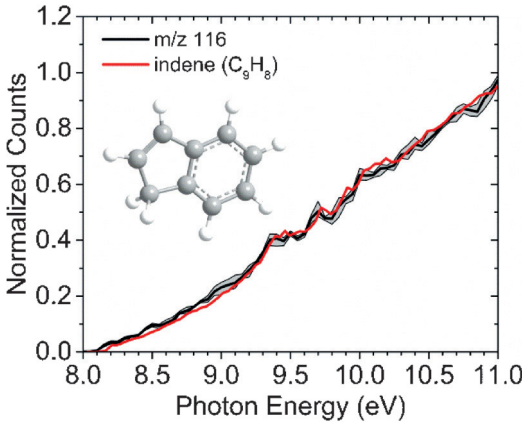

Figure 3. PIE curve recorded at $m/z=116$ shown as a black line, with experimental errors defined as a shaded area. The experimentally determined reference PIE curve of indene is shown as the red line.

experimentally determined PIE for indene (C_9H_8), as shown by the red line.[17] The PIE at $m/z=116$ was also tested for contributions from other C_9H_8 isomers (phenylallene, 1-phenyl-1-propyne, and 3-phenyl-1-propyne); however, these isomers possess ionization onsets much higher than that of indene (8.15 ± 0.05 eV). If formed, their contribution is less than 1%,[15a,18] therefore, we can conclude that the signal at $m/z=116$ originates solely from indene (C_9H_8), and not from other C_9H_8 isomers.

The experiments provide compelling evidence that indene (C_9H_8)—the prototype PAH carrying one six-membered and one five-membered ring—together with toluene (C_7H_8), are formed in the pyrolytic reactor under combustion-like conditions from the reaction of benzyl radicals with acetylene. What is the underlying reaction pathway to form the indene isomer? Previous electronic structure calculations[14] postulated that the acetylene molecule can add, together with a single carbon atom, to the CH_2 moiety of the benzyl radical via a barrier of 51 kJ mol^{-1} to form a doublet C_9H_9 intermediate (**1**), which is stabilized by 60 kJ mol^{-1} compared to the energy of the separated reactants (Figure 4). The doublet C_9H_9 intermediate (**1**) isomerizes through facile ring closure to the *ortho*-carbon of

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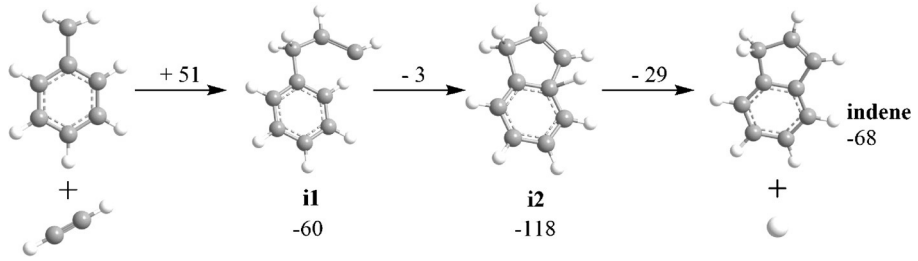

Figure 4. Schematic mechanism for the reaction of the benzyl radical with acetylene, leading to indene formation. The energies are relative to the reactants and are given in kJ mol^{-1}.

the phenyl ring over a barrier of 57 kJ mol^{-1}, which is slightly below the energy of the separated reactants, to form intermediate (**i2**); the latter is stabilized by 118 kJ mol^{-1} relative to the separated reactants. The bicyclic intermediate (**i2**) can be easily converted to the aromatic indene product by emitting a hydrogen atom from the *ortho*-carbon of the phenyl ring in an overall exoergic reaction (−68 kJ mol^{-1}). Note that toluene can be formed through the abstraction of a hydrogen atom, most likely from acetylene that is in excess, over a barrier of 87 kJ mol^{-1} in an overall exoergic reaction (−52.7 kJ mol^{-1}).[14] Likewise, the benzyl radical can react without an entrance barrier with atomic hydrogen, which is present in the reactor as a light byproduct of the benzyl plus acetylene reaction, to form toluene in the presence of a third-body collider. Accounting for the photoionization cross sections, we derive branching ratios of 99.5% versus 0.5% for indene versus toluene formation, that is, a dominance of the addition–cyclization–aromatization sequence, leading to indene. Previous kinetics experiments and computational investigations suggested a sequential mechanism for propargyl radical (C_3H_3) reaction with acetylene (C_2H_2) mediated by unidentified C_5H_5 and C_7H_7 species to form unassigned C_9H_8 isomer(s),[19] which have been identified as indene in the present study.

To summarize, the facile formation of indene (C_9H_8) through the bimolecular reaction of the benzyl radical (C_7H_7) with acetylene (C_2H_2) provides compelling evidence of the formation of the simplest PAH, carrying a six- and a five-membered ring, under combustion-like conditions. The high abundance of the aromatic and resonantly stabilized benzyl free radical together with acetylene in combustion flames promotes this reaction route as a predominant indene-formation channel in combustion environments.[5,20] Although mass-growth mechanisms to six-membered PAHs, such as naphthalene, through HACA have been well studied both computationally[10,21] and experimentally,[22] mechanisms reflecting facile five-membered aromatic-ring formation are less common. Here, the reaction of the benzyl radical with acetylene, leading to indene, could act as a versatile, mechanistic template to more complex PAHs containing five- and six-membered aromatic rings. Combustion environments are equally populated with methyl-substituted PAHs; each could undergo hydrogen abstraction to form a radical center at the exocyclic CH_2 moiety, thus creating an aromatic and resonantly stabilized benzyl-type free-radical reactant capable of propagating the acetylene-mediated formation of substituted indene-type PAHs.

Finally, the identification of a well-defined reaction pathway to indene holds important implications to the combustion chemistry community, as indene is considered as a building block and potential precursor to non-planar, bowl-shaped PAHs such as corannulene.[23]

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

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