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# **Molecular-Growth Pathways in Premixed Flames of**

# Benzene and Toluene doped with Propyne

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## Abstract

In a combined experimental and modeling effort, we investigated the molecular-growth pathways in propyne-doped low-pressure premixed flames of benzene and toluene. We determined the chemical structures of these two flames with flame-sampling molecular-beam mass spectrometry. The mole fraction profiles of the aromatic intermediates served as validation targets for two chemically detailed mechanisms that were independently developed at the German Aerospace Center (DLR) and at the Lawrence Livermore National Laboratory (LLNL). Reaction path analyses reveal the important pathways for indene, naphthalene, and phenanthrene. There is no appreciable fuel-structure effect and molecular growth was observed to be driven by radical-radical recombination reactions, and ring-closure and ring-enlargement reactions with little contribution from the classical HACA mechanism. Indene is formed in both flames through the reactions of the phenyl and propargyl radicals. The benzyl radical plays only a very minor role in the formation of indene through the reaction with acetylene. Reactions of the propargyl radical with fulvenallenyl, a C<sub>7</sub>H<sub>5</sub> isomer, contribute significantly to naphthalene formation in both flames investigated here. Benzyl radicals contribute to naphthalene formation via reactions with propargyl radical through formation of phenyl-substituted butadienyl and vinylacetylene isomers. Ring-enlargement reactions converting indene's five-membered ring into naphthalene's six-membered ring also contribute in small amounts to naphthalene. Fulvenallenyl radicals also contribute substantially to phenanthrene formation.

Keywords: premixed flames; indene; naphthalene; PAH formation; chemical modeling

## 1. Introduction

Aromatic species, ranging from single- and two-ring species to polycyclic aromatic hydrocarbons (PAHs), are important intermediates and precursors in the chemical reaction network of soot formation in combustion environments [1-7]. It is now well understood that the simplest aromatic species, benzene ( $C_6H_6$ ) or the respective phenyl radical ( $C_6H_5$ ), are formed through radical-radical and radical-molecule reactions of resonantly stabilized radicals [8, 9]. In many cases, the recombination reaction of two propargyl ( $C_3H_3$ ) radicals has been found to be important, but, depending on the fuel structure, other reactions, including *i*- $C_4H_5+C_2H_2$  and ring enlargement reactions, can also be of importance [10, 11].

Compared to the detailed understanding of benzene formation chemistry, the formation of larger aromatics, including the two-ring species indene (C<sub>9</sub>H<sub>8</sub>) and naphthalene (C<sub>10</sub>H<sub>8</sub>), is not yet fully understood. Indene is a two-ring aromatic species composed of fused benzene and cyclopentene rings. It is especially important to understand the formation chemistry of such fivemembered ring structures as found in indene and other cyclopenta-fused PAHs (CP-PAH), as they may be important for forming non-planar bowl-shaped PAHs [2]. Insights into the formation chemistry of indene, the simplest CP-PAH, might be helpful for understanding formation of other CP-PAHs, such as fluorene and acenaphthalene. Naphthalene is a two-ring aromatic species composed of two fused benzene rings. Understanding the formation of naphthalene is important to elucidate the fuel-structure dependence and identify repetitive reaction pathways for heavier peri-condensed PAHs, such as anthracene, phenanthrene, and pyrene molecular-weight growth in combustion processes. Many indene and naphthalene pathways have been proposed [12-34], although not comprehensively tested yet in flame chemistry modeling. It has been suggested that indene can be formed via radical-radical and radical-molecule reactions of  $C_5$ - $C_8$  species that contain five-and six-membered ring structures as building blocks:

$$C_5H_5$$
 (cyclopentadienyl) +  $C_4H_2$  (diacetylene) (1)

$$C_6H_5/C_6H_6$$
 (phenyl/benzene) +  $C_3H_3$  (propargyl) (2)

$$C_6H_5$$
 (phenyl) +  $C_3H_4$  (allene/propyne) (3)

$$C_6H_5/C_6H_6$$
 (phenyl/benzene) +  $C_3H_5$  (allyl) (4)

$$C_6H_5$$
 (phenyl) +  $C_3H_6$  (propene) (5)

$$C_6H_5CH_2$$
 (benzyl) +  $C_2H_2$  (acetylene) (6)

$$C_5H_4CCH_2/C_5H_4CCH$$
 (fulvenallene/fulvenallenyl) +  $C_2H_2$  (acetylene) (7)

$$C_8H_6$$
 (phenylacetylene) +  $CH_3$  (methyl) (8)

Furthermore, studies of the rearrangements on the  $C_{10}H_{11}$  potential energy surface were described in the literature investigating the indene formation mechanisms originating from the reactions of phenyl with 1,3-butadiene ( $C_4H_6$ ) and of cyclopentadiene ( $C_5H_6$ ) and cyclopentadienyl ( $C_5H_5$ ) [20, 21, 23]:

$$C_6H_5 + C_4H_6 (-CH_3)$$
 (9)

$$C_5H_6 + C_5H_5 (-CH_3)$$
 (10)

Reactions of the cyclopentadienyl with another cyclopentadienyl (or cyclopentadiene) also leads to formation of naphthalene [22, 25, 26]:

$$C_5H_5 + C_5H_5$$
 (or  $C_5H_6$ ) (11)

In addition to the hydrogen-abstraction- $C_2H_2$  addition (HACA mechanism) [27], other reactions that are typically considered for naphthalene formation include reactions of  $C_6H_5$  (or  $C_6H_6$ ), benzyl (fulvenallenyl), and indenyl ( $C_9H_7$ ) [12, 24, 28, 30-32, 35, 36]:

$$C_6H_5 \text{ (phenyl)} + i - C_4H_3 \tag{12}$$

$$C_6H_5$$
 (phenyl) +  $C_4H_4$  (vinylacetylene) (13)

$$C_6H_5 \text{ (phenyl)} + i-C_4H_5 \tag{14}$$

$$C_6H_6 \text{ (benzene)} + o-C_6H_4 \text{ (}o-\text{benzyne)} \tag{15}$$

$$C_5H_4CCH_2/C_5H_4CCH$$
 (fulvenallene/fulvenallenyl) +  $C_3H_3$  (propargyl) (16)

$$C_7H_7$$
 (benzyl) +  $C_3H_3$  (propargyl) (17)

$$C_9H_7$$
 (indenyl) +  $CH_3$  (methyl) (18)

To provide a comprehensive overview, these reaction pathways and the respective references for the kinetic data are summarized in tabular form in the Supplementary Material. Given these large sets of possible reactions leading to indene and naphthalene, it is unlikely that the formation of these simple two-ring aromatic species is dominated by one single reaction. In this work, we address this conceivable fuel-structure dependence by probing the importance of the reaction sequences of  $C_6H_5 + C_3H_3$  (2) and  $C_6H_5CH_2 + C_2H_2$  (6) for indene formation and of  $C_7H_7 + C_3H_3$  (17) and  $C_9H_7 + CH_3$  (18) for the formation of naphthalene and extend this work to elucidate the formation of phenanthrene. To this end, we studied the chemical structures of benzene and toluene low-pressure premixed flames which were doped with small amounts of propyne. This composition ensures that through H-abstraction reactions plenty of phenyl (from benzene), benzyl (from toluene), and propargyl (from propyne) are present in the reaction zone. As such, this study, which is based on earlier work on pure propyne [37-39], benzene and toluene

flames [40-44], helps to explore the role of the propargyl, phenyl, and benzyl radicals in growth of larger aromatic species in combustion environments. Parallel to the experimental analysis of the two flame structures, two chemically detailed mechanisms that have been described in Refs. [38] and [45] have been updated. Based on this mechanism, molecular level insights were gained into fuel molecular structure effects on the formation of indene and naphthalene.

## 2. Experimental procedures

The experiments were performed using the flame-sampling mass spectrometer at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory (LBNL). The experimental set-up has been described in detail before [46, 47]. Therefore, only a short description is given here.

The instrument consists of a flame-chamber in which the premixed flames are stabilized on a water-cooled stainless-steel McKenna-type burner at a pressure of 30 Torr (40 mbar). Gases from within the flames were extracted along the centerline of the flame via a quartz sampling probe (featuring an orifice diameter of 500  $\mu$ m) into a higher vacuum of a differentially pumped custom-built reflectron mass spectrometer. The pressure reduction from the flame chamber to the first pumping stage leads to the formation of a molecular beam and stops further reactions, thus allowing for the detection of short-lived intermediates. The molecular beam entered the ionization chamber through a nickel skimmer, located 23 mm downstream of the sampling nozzle. Ionization of the sampled flame gases was achieved via single-photon ionization by synchrotron-generated tunable vacuum-ultraviolet (VUV) radiation. This technique has been well established to provide information on the isomer-resolved identity of numerous chemical

intermediates, including radical species [46-48]. The mass spectrometer provides a mass resolution of m/ $\Delta$ m ~ 4000 and a sensitivity limit of ~1 ppm.

The two flames investigated here are characterized by the following flow and pressure conditions:

**Benzene-Propyne Flame:** 50% Ar, 40.5% O<sub>2</sub>, 4.1% benzene, 5.4% C<sub>3</sub>H<sub>4</sub> (propyne), p = 30 Torr, mass flux: 0.004032 g/cm<sup>2</sup> s<sup>-1</sup> (C/O ratio = 0.50; stoichiometry  $\phi$ = 1.6) **Toluene-Propyne Flame:** 50% Ar, 41.3% O<sub>2</sub>, 3.9% toluene, 4.8% C<sub>3</sub>H<sub>4</sub> (propyne), p = 30 Torr, mass flux: 0.00407 g/cm<sup>2</sup>s<sup>-1</sup> (C/O ratio = 0.46; stoichiometry  $\phi$  = 1.5)

The flame conditions were chosen as a compromise of a sufficient stand-off distance of the flame from the burner surface to allow for spatially resolved measurements, fuel-rich conditions to promote PAH growth chemistry, while minimizing visible flame perturbations by the sampling probe. The gas flows of Ar, O<sub>2</sub>, and C<sub>3</sub>H<sub>4</sub> were controlled using calibrated mass flow controllers. Benzene and toluene flows were measured using a syringe pump, quantitatively evaporated and added to the gas stream.

The multi-dimensional dataspace of mass spectra recorded at various positions away from the burner surface and at different photon energies was used to convert the data into mole fraction profiles of individual flame constituents. Different fixed soft ionization energies between 8.5 and 16.65 eV were used for the analysis of the flame. The data reduction procedures have been described before [14] and are not repeated here. The accuracy of the obtained mole fraction profiles depends on several factors and, as described in the literature, are expected to be in the order of 10-20% for the main species and within a factor of 2 for the intermediate species with known photoionization cross sections [46]. Photoionization cross sections are taken from [49] and the derived species mole fraction profiles are provided in the Supplementary Material.

The limitations of photoionization efficiency (PIE) curves, *i.e.*, mass-selected signal as a function of the photon energy, for the reliable identification of isomeric structures for large species have been discussed in Refs. [46, 47]. Therefore, we have not used PIE curves in this work for the identification of molecular-weight growth aromatics. Of particular importance for this work is the detection of phenyl-substituted, aliphatic C<sub>9</sub>H<sub>8</sub> isomers that has been qualitatively reported in Ref. [38].

The temperature profiles, which have been used as input parameters for the modeling calculations, were obtained by OH laser-induced fluorescence (LIF) using the frequency-doubled output of a dye laser (Sirah PrecisionScan) near 306 nm to excite the OH *A-X* (0,0) transition [50]. Following previously described routines [51], the measured temperature in the exhaust gas is folded with the sampling function obtained from the argon profile to obtain the perturbed temperature profile. This procedure has been shown to partially correct for the probeperturbation effects [52]. The temperatures used in the flame chemistry simulations are provided in the Supplementary Material.

## 3. Kinetic modeling

In an effort to provide an unbiased analysis of the importance of various reaction pathways of aromatic molecular-weight growth species, we used two independently developed detailed chemical mechanisms: a mechanism from the Lawrence Livermore National Laboratory (LLNL) and a mechanism from the German Aerospace Center (DLR). The basics of these two mechanisms have been described in detail in Refs. [38, 45]. The updates that were necessary to capture the chemistry in the two flames studied here, are described next. In addition to the benzene/toluene+propyne mixture flames described here, the two mechanisms were also used to predict the flame composition of pure benzene [41, 42], toluene [43, 44], and propyne premixed and counterflow flames [38, 39].

## 3.1 LLNL mechanism:

The LLNL mechanism used (see Supplementary Material) is an updated version of the LLNL's recent PAH mechanism [38, 53]. The original PAH mechanism of Ref. [38] was built using the molecular growth chemistry informed by recent kinetic studies from ab-initio and experimental methods [12, 21, 23, 24, 27, 28, 30-32], and already includes the molecular growth pathways R1-R18. However, several new kinetic studies have been published recently on the molecular growth and oxidation of aromatic species since the publication of mechanism of Ref. [38], and so the mechanism has been updated accordingly to incorporate the latest understanding of the chemistry. The major changes to the chemistry include a) oxidation of phenyl radical ( $C_6H_5$ ) by O<sub>2</sub> [54], b) oxidation of fulvenallenyl radical by O<sub>2</sub> and O, d) using a simplified description of the recombination reaction of cyclopentadienyl radicals [59], e) ring-expansion reactions of methyl-radical with acenaphthyl radicals ( $C_{12}H_7$ ) to produce phenalene and its radical [60], f) reactions of acenaphthyl radicals with acetylene [61], g) reaction of phenyl radicals with phenylacetylene

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[62], i) reactions of CH<sub>3</sub> with resonantly stabilized cyclohexadienyl radical, j) reactions of resonantly stabilized fluorenyl radical with CH<sub>3</sub>. Changes (a)-(g) pertain to adopting the new reactions channels and the associate rate parameters from ab-initio studies into the mechanism. Changes (i) and (j) were done to describe reactions of methyl radical with resonantly stabilized cyclohexadienyl and fluorenyl radical based on  $C_5H_5+CH_3$  potential energy surface (PES).

Of the several updates, updates to the  $C_6H_5 + O_2$  system had a strong effect on the flame structure predictions. This strong effect can be attributed to several reasons which include: importance of the oxidation of phenyl radical in oxidation chemistry of benzene and toluene, the lack of comprehensive understanding of the oxidation of phenyl radical by  $O_2$  in the literature, missing pathways in the earlier mechanism which effect the chain branching and chain propagating nature of this reaction system. Considering the importance of these changes, we have also updated the description of the oxidation chemistry of naphthyl radical to ensure internal consistency in kinetic mechanism. Furthermore, in our prior work on  $C_3H_4$  flames [38] and pyrolysis of gasoline surrogates [53],  $C_7H_5$  (fulvenallenyl), and  $C_9H_7$  (phenyl-propargyl and indenyl radicals) have been shown to play an important role in molecular growth. As molecular growth is sensitive to flux through oxidation chemistry, we have updated the oxidation chemistry of  $C_7H_5$  and  $C_9H_7$  radicals using analogies with oxidation of propargyl and cyclopentadienyl radicals. Furthermore, the mechanism also includes several updates to the pyrolysis chemistry of xylene and trimethylbenzene isomers which are not important here and shall be a subject of future publications.

#### **3.2 DLR LPF mechanism:**

The mechanism developed at the DLR (referred to as DLR LPF (low-pressure flame)) and used in the present work is an extended version of the model recently proven to be capable to model the oxidation of mixtures of 1,3-butadiene/*iso*-butanol [63] and of 1,3-butadiene/*n*-butanol [29] in low pressure flames. This starting mechanism consists of 286 species connected via 1396 reactions. Earlier versions of this reaction mechanism, which includes soot precursors and aromatics [64, 65], were shown to describe sufficiently the oxidation of propene [66] and cyclopentene [67] in low-pressure flames.

For this study, first a more detailed description of the reaction network of phenylacetylene, indene, acenaphthalene, and naphthalene was included as being part e.g., within the recent developed reaction model by Kathrotia et al. [68]. Secondly, the reactions currently discussed for their potential of contributing within the formation of indene and naphthalene as described in the introduction have been included. The detailed and extensive work from the groups of Mebel and Kaiser served as a guidance for the rate expressions.

Furthermore, the consumption pathway of the benzyl radical turned out to play a pivotal role within the formation of the two-ring aromatics. Here, the reaction of benzyl to fulvenallene (+H) and finally to fulvenallenyl radical ( $C_7H_5$ ) was the source for the enhanced production of naphthalene via reaction (16). The description of this benzyl decomposition pathways was first suggested in Ref. [69], but seemed to be impossible at that time due to the unavailability of thermodynamic data.

However, in view of the large number of isomers, in particular for the large hydrocarbons involved, and their resulting huge reaction network a full implementation into the DLR reaction mechanism was out of scope. A strategy to circumvent this challenge requires adapting reactions including their rate reaction expressions according to the lumping approach [45]. This approach has been guided by our intention to keep the reaction mechanism as compact as possible; this means a balance between the performance of the model with respect to its predictability of the specific target - here, the two-ring aromatics indene and naphthalene - and the time efforts to run the model. Such a reduced mechanism is crucial for numerically aided designs of new engines in order to reduce the time consumed by chemical kinetic calculations within the computational fluid dynamics (CFD) modeling.

The updated chemical-kinetic reaction DLR LPF mechanism consists of 288 species and 1505 elementary reactions, with 3 species (phenylpropyne, fulvenallene, fulvenallenyl) and 109 reactions newly added.

Computer simulations of the isobaric burner-stabilized flames were performed with the open-source software Cantera [70] using the experimental temperature profiles (without any shifts). In addition, initial mass flow rates and composition of the reactants as well as the burner's diameter served as further input data. For the simulations, the multi-component diffusion model and thermo-diffusion were considered. The used transport data were based on the Chemkin Transport Database [71], the thermodynamical data were based from Ref. [72].

## 4. Results and discussion

Both mechanisms accurately capture the mole fraction profiles of the main species ( $H_2$ ,  $H_2O$ , CO, O<sub>2</sub>, C<sub>3</sub>H<sub>4</sub>, Ar, CO<sub>2</sub>, benzene/toluene) and common intermediates. These comparisons are shown in the Supplementary Material. The overall performance of both chemical mechanisms

provides evidence for a satisfactorily description of the flame chemistry. Some discrepancies near the burner surface are likely to be caused by the uncertainty in the temperature profile originating from sampling probe perturbations [46, 52].

It is understood that in typical high-temperature combustion processes, intermediate species yielded from fuel decomposition, i.e. phenyl, benzyl, and propargyl in this study, are the initial gas-phase building blocks for the formation of PAHs [8]. Here, we discuss how different fuel structures influence the importance of the intermediate species pool and ultimately the formation pathways of aromatic species contributing to soot formation via molecular-weight processes. It is thus instructive in a first step to analyze the recorded mass spectra of the different flames.

A representative mass spectrum is shown in Fig. 1. It provides a general overview of signals at a variety of mass-to-charge (m/z) ratios between 110 and 210 after sampling from the reaction zone at 3.25 mm above the burner surface in the toluene-propyne flame. Synchrotron-generated photons of 10.5 eV were used as this energy is sufficient to ionize the aromatic species, while at the same time dissociative ionization processes are minimized. The mass progression of the signals between m/z = 116 (C<sub>9</sub>H<sub>8</sub> isomers, e.g. indene) and 202 (C<sub>16</sub>H<sub>10</sub>, e.g. pyrene) includes progressions of C<sub>x</sub>H<sub>8</sub>, C<sub>x</sub>H<sub>10</sub>, C<sub>x</sub>H<sub>12</sub>. As pointed out earlier [73, 74], these observed patterns are an indication of repetitive reaction sequences. Overall, similar mass spectra are sampled from the toluene-propyne and benzene-propyne flames, although signal intensities for the molecular-weight growth intermediates are consistently larger in the toluene-base flame despite a slightly smaller C/O ratio and stoichiometry. Compared to mass spectra recorded previously after sampling from allene and propyne flames [38, 39], the mass spectra recorded here exhibit striking

similarities of the peaks, although differences of the relative intensities of the intermediates are obvious. As shown in Refs. [74, 75], these different intensities allow for extraction of fuelstructure specific chemistries. Here, contributions from the benzyl radical in the toluene/propyne flame can be seen in the intense peaks at m/z = 168 and 182, which likely result from the benzyl + phenyl [76] and benzyl + benzyl reactions, respectively. The strong signal at m/z = 144 is an oxygen-containing C<sub>10</sub>H<sub>8</sub>O species, probably a naphthol isomer. While some important features of the propargyl, phenyl, and benzyl reaction network are immediately visible from the mass spectra, additional features can be extracted in combination with flame-chemistry modeling and subsequent reaction path analysis.

The peak intensities of the multiple mass spectra (as a function of distance from the burner and photon energy) have been converted into mole fraction profiles of 20 aromatics (m/z



Figure 1: Overview mass spectrum from m/z = 110-210 after sampling at 3.25 mm above the burner surface from the toluene-propyne flame using 10.5 eV photons for ionization. The observed peaks belong to various aromatic ring species.

between 78 and 204), see the Supplementary Material. In Fig. 2, we show a comparison between the experimentally observed maximum concentrations of aromatic species in (a) the benzenepropyne and (b) the toluene-propyne flames with the predicted results from the two mechanisms.

Overall, a reasonable agreement of the predicted and simulated peak mole fractions can be observed; however, some differences are clearly identifiable. For example, the DLR LPF mechanism underpredicts the maximum mole fraction of toluene in the benzene flame by about a factor of 3, while the predicted toluene profile from the LLNL mechanism captures the peak concentration quite accurately. An overprediction of the DLR LPF mechanism is visible for  $C_{12}H_8$ (acenaphthylene), in both flames. It is also noted that, although on average better in the predictions, the LLNL mechanism is consistently underpredicting the observed species mole fractions. The differences in predicted mole fractions for most species are within a factor of two while higher differences are observed in the case of  $C_8H_{10}$  (ethylbenzene or xylene isomers),  $C_8H_8$ (styrene),  $C_8H_6$  (phenylacetylene), and  $C_9H_{12}$  (trimethyl benzene, ethyl toluene isomers).  $C_8H_{10}$ and  $C_9H_{12}$  could be produced from successive methylation of the aromatic ring or through



Figure 2: Comparison of the experimental peak mole fraction of different aromatic intermediates with their simulated mole fractions. (a) benzene+propyne flame. (b) toluene+propyne flame.

reactions of benzylic radical with CH<sub>3</sub> radicals. The reaction rate for methylation of the aromatic ring:  $C_6H_5 + CH_3 =$  toluene,  $C_6H_5 + CH_3 =$  benzyl + H,  $C_6H_6 + CH_3 =$  toluene + H have been adopted from recent ab-initio studies [77, 78]; the uncertainty in the rate parameters is expected not to be large. However, the temperature and pressure dependence of reactions of benzylic radicals with CH<sub>3</sub> (e.g., benzyl + CH<sub>3</sub> = ethylbenzene, xylyl + CH<sub>3</sub> = ethyl toluene) to our knowledge have not been studied theoretically and the lack of rigorous characterization of temperature and pressure dependence is a plausible reason for the underprediction of these methylated aromatics by the LLNL mechanism. Furthermore, in the simulations with the LLNL mechanism, sequential H<sub>2</sub> eliminations from ethylbenzene were found to be important for production of  $C_8H_8$  (styrene) and the underprediction of  $C_8H_{10}$  and  $C_8H_8$  are linked. The differences observed in predictions of  $C_8H_6$  is currently not clear, and rather surprising as its formation has been modeled based on recent ab-initio studies [27, 31] in the LLNL mechanism.

While Fig. 2 provides an overview of the observed and predicted maximum aromatic intermediate mole fractions, Fig. 3 explicitly shows the experimental and predicted mole fraction profiles for  $C_9H_8$  (indene + phenylpropynes + phenylallene + methyl-phenylacetylene),  $C_{10}H_8$  (naphthalene + benzofulvene + phenyl substituted-vinylacetylenes), and  $C_{14}H_{10}$  (anthracene/phenanthrene + ethynyl-biphenyl + diphenylacetylene) for both the benzene-propyne and toluene-propyne flames. Figure 3 allows assessment of the predictive capabilities of both mechanisms in more detail by taking the profile shapes in account as well.

A few observations can be made: a) For the benzene-propyne flame, both the LLNL and the DLR LPF mechanisms results are in reasonable agreement with the experimental results for the C<sub>9</sub>H<sub>8</sub> and C<sub>10</sub>H<sub>8</sub> isomers; with the DLR LPF mechanism predicting the peak mole fraction and position very accurately. b) The DLR LPF mechanism consistently overpredicts the intermediate concentrations in the toluene-propyne flame, indicating that either the precursor formation chemistry or the PAH chemistry is not captured accurately. Also, the peak position of C<sub>10</sub>H<sub>8</sub> in the toluene-propyne flame is not captured correctly in the DLR LPF mechanism. This observation may reflect the exclusion of the bundle of isomers and their reaction network reaction pathways in the DLR mechanism. c) The simulated profile shape of the C<sub>14</sub>H<sub>10</sub> in the DLR LPF mechanism indicates that the oxidation steps might not be covered accurately.



Figure 3: Plot comparing the experimental and simulated profiles of  $C_9H_8$  [(a)+(b)],  $C_{10}H_8$  [(c)+(d)], and  $C_{14}H_{10}$  [(e)+(f)] in the premixed benzene-propyne flame (left column) and toluene-propyne flame (right column).

## 5. Kinetic analyses

Next, we describe the elucidation of the reaction path analysis for indene, naphthalene, and phenanthrene in both, the benzene-propyne and toluene-propyne flames. To allow for a comprehensive discussion, we focus only on the results from the LLNL mechanism for the remainder of this paper. This focus on the LLNL mechanism can be justified with the overall slightly better performance of the mechanism and the more detailed description of the PAH reaction network. With the focus of the paper on the elucidation of the indene, naphthalene, and phenanthrene pathways, a detailed comparison of the two different mechanisms is beyond the scope of the present paper. The interested reader is referred to the Supplementary Material that contains the results of the reaction path analysis using the DLR LPF mechanism. In short, for the indene and naphthalene formation pathways the ROPs of the DLR LPF and LLNL mechanism show some clear differences, although the C<sub>7</sub>H<sub>5</sub> chemistry for naphthalene formation is highlighted in both mechanisms (see below). These observations are in agreement with earlier work, in which it was shown that chemical mechanisms with comparable predictive capabilities can lead to largely different reaction path analysis [79]. In summary, the DLR LPF results mirror the simplified/lumped description of the molecular-weight growth PAH chemistry, while, at the same time, identify the limits of this lumping approach.

The Supplementary Material also includes a visual summary of the LLNL mechanism's performance compared to the pure benzene and toluene flames and the analyses of the reaction pathways for indene, naphthalene, and phenanthrene in those flames.

#### 5.1 Phenyl and benzyl consumption:

To understand the indene and naphthalene formation in the benzene-propyne and toluenepropyne flames, it is important to understand the reaction flux through the phenyl and benzyl radicals, respectively. For the reaction path analysis discussed next, we integrated the flux from 0-3 mm HAB. According to the LLNL mechanism, and as shown in Fig. 4, in both flames phenyl (C<sub>6</sub>H<sub>5</sub>) is largely (>55%) consumed through oxidation reactions with O<sub>2</sub>, and only small amounts of C<sub>6</sub>H<sub>5</sub> are consumed via molecular-growth reactions with methyl and propargyl radicals. The main products of phenyl oxidation are 2,4-cyclopentadione (C<sub>5</sub>H<sub>4</sub>O) + formyl radical (HCO) followed by phenoxy + O. Only small amounts of phenyl are found to participate in moleculargrowth pathways via reactions with methyl and propargyl radicals. The reactions of C<sub>6</sub>H<sub>5</sub> with CH<sub>3</sub> lead to the formation of benzyl (C<sub>6</sub>H<sub>5</sub> + CH<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> + H) and toluene (C<sub>6</sub>H<sub>5</sub> + CH<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) in



Figure 4: Phenyl (top) and benzyl (bottom) radical consumption in the benzene-propyne and toluenepropyne flames, respectively.

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the benzene flame, with a relatively higher flux formation of  $C_6H_5CH_2$ . Interestingly, the reaction  $C_6H_5 + CH_3 = C_6H_5CH_2 + H$ , was observed to consume benzyl radicals in the toluene-propyne flame and acts as a minor pathway for production for  $C_6H_5$ .

The main pathways for consumption of benzyl radicals were found to be termination reactions with H-radicals producing toluene followed by oxidation reactions with O atoms, and chain termination reactions with methyl radicals producing ethylbenzene ( $C_6H_5CH_2 + CH_3 = C_6H_5C_2H_5$ ). The other molecular growth pathways involving benzyl radicals were found to be radical-radical recombination reactions with vinyl ( $C_2H_3$ ), propargyl ( $C_3H_3$ ), and phenyl ( $C_6H_5$ ) radicals producing 3-phenyl-1-propene ( $C_6H_5CH_2 + C_2H_3 = C_6H_5C_3H_5$ ), phenyl-butadiene isomers ( $C_6H_5CH_2 + C_3H_3 = A1CCVCVC/A1CCCTC$ ), and diphenylmethane ( $C_6H_5CH_2 + C_6H_5 = C_6H_5CH_2C_6H_5$ ).

#### 5.2 Indene formation:

In the ROP analysis (Supplementary Material), indene production pathways in both the flames were found to be similar and largely controlled by the recombination reaction between phenyl and propargyl radicals. The reaction sequence for production of indene can be summarized by Fig. 5. As seen in Fig. 5, there is a lack of direct pathway for formation of indene from phenyl, and indene formation rather proceeds in two-steps. The first step is the formation of aliphatic C<sub>9</sub>H<sub>8</sub> isomers and indenyl radical from C<sub>6</sub>H<sub>5</sub> + C<sub>3</sub>H<sub>3</sub> recombination reaction, and the second step is Hassisted conversion of aliphatic C<sub>9</sub>H<sub>8</sub> isomers and indenyl radical to indene. The ROP analysis of indene shows the recombination of indenyl radical with H-radical to be the main source of indene. However, indenyl radical is observed to be produced predominantly from H-abstraction reactions from indene. This shows that production of indene and indenyl radical are closely coupled and the chemistry important for formation of indene and its radical can be mainly attributed to  $C_6H_5 + C_3H_3$  reaction (as summarized in Fig. 5). Furthermore, the ROP analysis shows very little contribution of reactions between acetylene and benzyl radical ( $C_6H_5CH_2 + C_2H_2 =$ indene + H) towards formation of indene in both the flames. The reaction path analysis for both, the benzene-propyne and the toluene-propyne flame, are very similar, i.e., the same reactions contribute in both flames and there seems to be no significant fuel-structure dependence on the importance of these pathways. This finding is consistent with earlier work [74, 80].

It is important to note, that especially in the toluene-propyne flame, contributions from the benzyl radical (and its isomer fulvenallenyl) with acetylene, i.e., reactions 6 and 7, are found not to be important molecular-weight growth pathways. Indeed, reactions 6 is found to contribute more to the consumption than to production of indene beyond 3 mm (not shown here). Furthermore, reaction 8, phenylacetylene + CH<sub>3</sub>, is also not contributing significantly to molecular-weight growth. It is to be noted that the rate parameters for reaction 8 in LLNL



Figure 5: Graphical visualization of indene and indenyl formation pathways in the benzene-propyne and toluene-propyne flame. Results are based on the LLNL mechanism.

mechanism has been adopted from recent work of Mebel et al. [29] and was found to be substantially lower than estimates used in literature mechanisms.

#### 5.3 Naphthalene Formation:

While for indene formation only a very limited number of pathways are found to be important, the situation is more complex for naphthalene with comparable contributions from several reactions. As seen in Fig.6, naphthalene can be produced from several reactions which include: dialin radicals ( $C_{10}H_9$ ), fulvenallenyl ( $C_7H_5$ ) + propargyl reaction, benzofulvene (CH2IND) + H, A1CVCCTC + H etc. The fulvenallenyl ( $C_7H_5$ ) + propargyl reaction has been proposed to proceed similar to the  $C_3H_3$  +  $C_3H_3$  reaction leading to the direct formation of naphthalene/benzofulvene/naphthalene radicals [12]. Instead, the formation of naphthalene from  $C_{10}H_9$ ,  $CH_2IND$ ,  $C_9H_6CH_3$ , A1CVCCT was found to involve a complicated reaction network initiated by two other reactions benzyl +  $C_3H_3$  and indenyl ( $C_9H_7$ ) +  $CH_3$ . These two reactions involve radical-radical recombination and ring-enlargement reaction. The details of the reaction sequence indenyl ( $C_9H_7$ ) +  $CH_3 \rightarrow C_9H_7CH_3 \rightarrow C_9H_6CH_3/C_9H_7CH_2 \rightarrow benzofulvene (CH2IND) + H <math>\rightarrow$ 



Figure 6: ROP analysis showing the important pathways for production of naphthalene in the benzene-propyne flame.

naphthalene + H can be found in our earlier works and also in that of Zhao et al. [36], and so we turn our attention on the reaction sequence of benzyl +  $C_3H_3$ .

The reaction sequence initiated by benzyl + C<sub>3</sub>H<sub>3</sub> recombination reaction has been summarized in Fig. 7 and starts with formation of but-3-yn-1ylbenzene (A1CCCTC) and buta-2,3-dien-1-ylbenzene(A1CCVCVC). These isomers could either undergo unimolecular ring-closure reactions to produce naphthalene (via formation of diradicals) [30] or could isomerize to buta-1,3-dien-1-ylbenzene (A1C4H5) via unimolecular or H-assisted isomerizations. Owing to the abundance of H-radicals in the premixed flames and also due to the low reaction rates for their unimolecular ring-closure reactions to produce naphthalene [30], A1CCCTC and A1CCVCVC are observed to be converted to A1C4H5. A1C4H5 can undergo a ring-closure ring reaction to produce 1,4-dihydronaphthalene or participate in H-abstractions followed by H-elimination to



Figure 7: Formation of naphthalene from benzyl + propargyl reactions.

produce phenyl-vinylacetylenes (A1CTCCVC or A1CVCCTC). These phenyl-substituted vinyl acetylenes participate in H-assisted isomerizations to produce naphthalene as shown by Zhao et al. [32]. 1,4-dihydronaphthalene participates in H-abstraction reactions to produce dialin radicals  $(C_{10}H_9)$ , which subsequently undergo H-elimination to produce naphthalene.

The overall chemistry relevant to formation of naphthalene can be summarized by Figure 8. Here, the main role of reactions with propargyl radicals and fulvenallenyl /fulvenallene molecules involved should be highlighted as these are the major formation route. Contributions from cyclopentadienyl radicals to naphthalene formation are not significant in the flames studied here.

#### 5.4 Formation of Phenanthrene:

In the ROP analysis, the reaction pathways important for formation of phenanthrene were found to be similar in both the flames and can be summarized using the reactions shown in Fig. 9. The conversion of fluorene ( $C_{13}H_{10}$ ) to phenanthrene via ring expansion reactions of the fluorenyl ( $C_{13}H_{9}$ ) with methyl was found to be the main pathway in both flames. This ring expansion



Figure 8: Simplified description for formation of naphthalene.

reaction of fluorene to produce phenanthrene is similar to that of formation of naphthalene from indene. Fluorene in the present flames appears to be produced from reactions of phenyl with benzyl:  $C_6H_5CH_2 + C_6H_5 = C_{13}H_{12}/C_{13}H_{11} + H$ ,  $C_{13}H_{12} = C_{13}H_{11} + H$ ,  $C_{13}H_{11} = C_{13}H_{10} + H$ ).

The self-recombination reaction of fulvenallenyl radicals to produce phenanthrene was found to be the second important pathway in toluene- $C_3H_4$  flame, while the reactions of *o*-biphenyl ( $C_{12}H_9$ ) with acetylene was found to be the second most important pathway in benzene- $C_3H_4$ flame. The LLNL mechanism predicts the concentration of fulvenallene ( $C_7H_6$ ) and its radical ( $C_7H_5$ ) to be larger in the toluene flame by about a factor of 3, while the predicted concentration of biphenyl ( $C_{12}H_{10}$ ) does not change significantly (difference less than 10%). This difference in relative concentrations of  $C_7H_5$  and  $C_{12}H_{10}$  could be the reason for the change in relative importance of these pathways towards formation of phenanthrene in the benzene and toluene flames.

These three pathways (fluorenyl +  $CH_3$ ,  $C_7H_5$  +  $C_7H_5$ ,  $C_{12}H_9$  +  $C_2H_2$ ) were found to contribute to more than 70% production of phenanthrene in both the flames. The other minor pathways for



Figure 9: Simplified description of the pathways important for formation of phenanthrene in toluene-C<sub>3</sub>H<sub>4</sub> and benzene+C<sub>3</sub>H<sub>4</sub> flame. formation of phenanthrene in the present flames include ipso-substitution reactions of methylphenanthrene with H radicals ( $CH_3-C_{14}H_9 + H = C_{14}H_{10} + CH_3$ ), ring expansion reactions of benzoindenes ( $C_{13}H_{10}$ ) with methyl radicals, H-assisted isomerization of *o*-ethynylbiphenyl produced from  $C_6H_5C_2H + C_6H_5$  reaction and hydrogen eliminations from diphenylethylene.

## 6. Conclusions

This work reveals the molecular-growth pathways of aromatic species in propyne-doped lowpressure premixed flames of benzene and toluene. These fuels, and their combination, are especially of importance because key radicals, i.e., propargyl, phenyl, and benzyl, are formed in larger concentrations directly from the fuels through H-abstraction reactions.

For the formation of indene, the reaction path analysis revealed the importance of the propargyl and phenyl-substituted propargyl radicals in both flames. Because of the dominance of this reaction network, it can be anticipated that fuel-structure effects on the importance of the various pathways are only minimal. Indeed, we found that, when comparing the reaction pathways for the formation of indene in the flames studied here with the pure benzene [42], toluene [43, 44], and propyne flame [38], indene formation is dominated by the phenyl plus propargyl reaction. Although, it should be highlighted that our findings here are slightly different than the modeling results from Refs. [42, 44].

The situation for the naphthalene formation is more complex. Several pathways with comparable fluxes contribute and we predict that their respective importance varies slightly with the fuel-structure. Most important reactions include the ring-enlargement reaction converting the cyclopenta-fused indene, the benzyl plus propargyl reaction that proceeds via phenylsubstituted butadienyl radicals and/or phenyl-substituted vinylacetylene, and reactions of fulvenallenyl radicals with propargyl. The role of the fulvenallenyl radical is peculiar, as it is not just formed through isomerization/dehydrogenation of the benzyl radical, but through the growth reaction of propargyl with diacetylene [81] and oxidation reactions of phenylacetylene. We note that the original HACA mechanism contributes only little to the naphthalene formation in these flames. When comparing with the naphthalene formation to the pure benzene, toluene, and propyne flames, the mechanism predicts that the importance of the various reaction pathways slightly changes and that the addition of propyne enhances the importance of the benzyl+propargyl reaction as described in Fig. 7.

Furthermore, a literature review reveals the fuel-structure dependence of the importance of the indene and naphthalene formation pathways. For example, naphthalene formation through cyclopentadienyl radical recombination has been found to be dominant in cyclopentene and 1-pentene flames [10, 82]. It remains intriguing that, despite the diverse portfolio of different reaction and reaction classes, similar signal and intensity patterns can be observed in the mass spectra [73, 74, 80, 83]. The formation of larger cyclopenta-fused PAHs (beyond indene) and larger peri-condensed PAHs (beyond naphthalene) via analogous reactions discussed here should be tested in future work.

From analysis of formation of indene, naphthalene and phenanthrene, it can be inferred that the important molecular growth pathways include a) radical-radical recombination reactions of resonantly stabilized radicals with aromatic radicals (e.g.,  $C_6H_5 + C_3H_3$ ,  $C_6H_5CH_2 + C_6H_5$ ), b) recombination reactions of propargyl-like radicals ( $C_7H_5 + C_7H_5$ ,  $C_7H_5 + C_3H_3$ ), c) ring enlargement reactions of intermediates produced from recombination reactions of methyl radicals with resonantly stabilized cyclopentadienyl like radicals ( $C_5H_5 + CH_3$ ,  $C_9H_7 + CH_3$ ,  $C_{13}H_9 + CH_3$ ), and d) HACA pathways. Overall, the reaction network for molecular growth from benzene to phenanthrene could be simplified as shown in Fig. 10.

It should be kept in mind that the presented reaction path analyses are dependent on the chemical kinetic mechanism that is used to describe the combustion chemistry. Previous work clearly showed that different mechanisms can predict different reaction fluxes while, at the same time, achieving satisfactory agreement between experiment and model predictions [79]. Therefore, including the latest and most accurate reaction rate constants and thermodynamical data in these mechanisms ensures that the mechanism predicts the reaction flux and the importance of the various proposed pathways to the best of the community's current knowledge.



Figure 10: Simplified visualization of the molecular-growth reaction network in the benzene-C<sub>3</sub>H<sub>4</sub> and toluene-C<sub>3</sub>H<sub>4</sub> flames studied here.

While this paper almost entirely focused on molecular-growth pathways, it is important to consider that the observed species' mole fraction profiles are a combination of growth and oxidation reactions. Oxidation mechanisms of PAHs should be addressed in future work.

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# Supplementary Material

for

# **Molecular-Growth Pathways in Premixed Flames of**

## Benzene and Toluene doped with Propyne

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## Table 1: Proposed Reaction Pathways leading to indenyl/indene and naphthyl/naphthalene

$C_5H_5$ (cyclopentadienyl) + $C_4H_2$ (diacetylene)	
$C_6H_5/C_6H_6$ (phenyl/benzene) + $C_3H_3$ (propargyl)	[1-3]
$C_6H_5$ (phenyl) + $C_3H_4$ (allene/propyne)	[1, 2, 4]
$C_6H_5/C_6H_6$ (phenyl/benzene) + $C_3H_5$ (allyl)	[1-4]
$C_6H_5$ (phenyl) + $C_3H_6$ (propene)	[1, 2, 4]
$C_6H_5CH_2$ (benzyl) + $C_2H_2$ (acetylene)	[2, 4, 5]
$C_5H_4CCH_2/C_5H_4CCH$ (fulvenallene/fulvenallenyl) + $C_2H_2$ (acetylene)	[6, 7]
$C_8H_6$ (phenylacetylene) + CH <sub>3</sub> (methyl)	[2]
$C_6H_5 + C_4H_6$ (-CH <sub>3</sub> )	[8, 9]
$C_{5}H_{6} + C_{5}H_{5}$ (-CH <sub>3</sub> )	[1, 10]
$C_5H_5 + C_5H_5$ (or $C_5H_6$ )	[4, 10-13]
$C_6H_5$ (phenyl) + $C_4H_4$ (vinylacetylene)	[4, 14, 15]
C <sub>6</sub> H <sub>6</sub> (benzene) + <i>o</i> -C <sub>6</sub> H <sub>4</sub> ( <i>o</i> -benzyne)	[16]
$C_5H_4CCH_2/C_5H_4CCH$ (fulvenallene/fulvenallenyl) + $C_3H_3$ (propargyl)	[17]
$C_7H_7$ (benzyl) + $C_3H_3$ (propargyl)	[2, 4, 5, 16]
$C_9H_7$ (indenyl) + CH <sub>3</sub> (methyl)	[2, 4, 18-20]

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