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A VUV Photoionization Study of the Formation of The Indene Molecule and its Isomers

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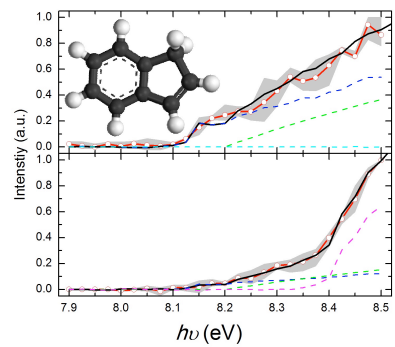
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Key words:

Indene, polycyclic aromatic hydrocarbons (PAHs), photoionization efficiency (PIE), vacuum ultraviolet (VUV) radiation, ab initio calculation.

ABSTRACT The aromatic indene molecule (C_9H_8) together with its acyclic isomers (phenylallene, 1-phenyl-1-propyne, and 3-phenyl-1-propyne) were formed via a ‘directed synthesis’ *in situ* utilizing a high temperature chemical reactor under combustion-like conditions (300 Torr, 1,200-1,500 K) through the reactions of the phenyl radical (C_6H_5) with propyne (CH_3CCH) and allene (H_2CCCH_2). The isomer distributions were probed utilizing tunable vacuum ultraviolet (VUV) radiation from the Advanced Light Source by recording the photoionization efficiency (PIE) curves at mass-to-charge of $m/z = 116$ ($C_9H_8^+$) of the products in a supersonic expansion for both the phenyl-allene and phenyl-propyne systems; branching ratios were derived by fitting the recorded PIE curves with a linear combination of the PIE curves of the individual C_9H_8 isomers. Our data suggest that under our experimental conditions, the formation of the aromatic indene molecule via the reaction of the phenyl radical with allene is facile and enhanced compared to the phenyl –propyne system by a factor of about seven. Reaction mechanisms and branching ratios are explained in terms of new electronic structure calculations. Our newly developed high temperature chemical reactor presents a versatile approach to study the formation of combustion-relevant polycyclic aromatic hydrocarbons (PAHs) under well-defined and controlled conditions.

The energetics and dynamics of the reactions of aromatic radicals (ARs) such as the phenyl radical (C_6H_5) with unsaturated hydrocarbons are of paramount importance in untangling the formation of polycyclic aromatic hydrocarbons (PAHs) from the ‘bottom up’ in combustion flames^{1,2} and in carbon-rich circumstellar envelopes.³ Due to their inherent thermodynamical stability, ARs can reach high concentrations in flames; this makes them important reactants to be involved in the formation of PAHs and carbonaceous nanostructures. Reaction mechanisms are suggested to involve ARs like phenyl⁴ with unsaturated C3 and C4 hydrocarbons possibly forming bicyclic aromatic hydrocarbon molecules with indene (C_9H_8) and naphthalene ($C_{10}H_8$) cores. However, no experiment has been conducted so far in which a PAH (like) species is formed as a result of a *directed* and *controlled* synthesis in the gas phase under combustion-like conditions. Computational predictions do exist. For instance, Fascella et al.⁵ investigated the reaction of the phenyl radical with 1,3-butadiene (C_4H_6) theoretically suggesting that over the complete temperature range of 500–2,500 K, 1,4-dihydronaphthalene ($C_{10}H_{10}$) was the predominant product. Considering the indene molecule (C_9H_8), Vereecken et al.⁶⁻⁸ estimated theoretically the product distributions of the reactions of phenyl with propyne (CH_3CCH) and allene (H_2CCCH_2). The authors proposed that indene should be the dominant product at low pressures and temperatures up to 500 K (Figure 1). At higher temperatures of up to 2,000 K, the branching ratios strongly depend on the pressure (1 – 100 atm) and effective temperature leading to C_9H_8 isomers indene, 1-phenyl-1-propyne, 3-phenyl-1-propyne, and phenylallene; additional exit channels of phenylacetylene (C_6H_5CCH) plus the methyl radical (CH_3) and benzene (C_6H_6) plus the propargyl radical (H_2CCCH) were also proposed. At temperatures of 3,000 to 4,000 K, indene was found to be only a small fraction of all products formed. The latter finding is consistent with recent crossed molecular beam experiments conducted at collision energies of about 150 kJmol^{-1} suggesting that 1-phenyl-1-propyne and phenylallene are the dominating C_9H_8 isomers formed in the reactions of phenyl radicals with propyne and allene, respectively, under single collision conditions.⁹

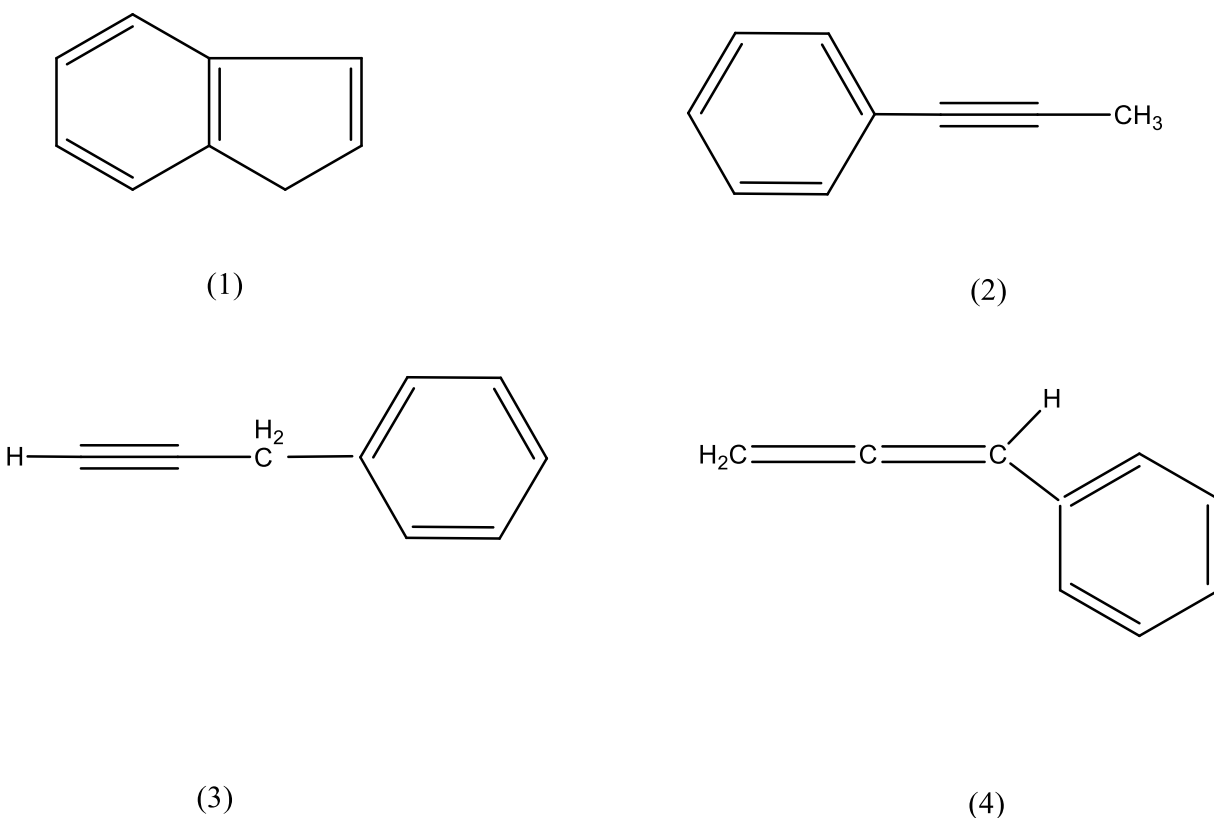


Figure 1: Structures of distinct C_9H_8 isomers: indene (1), 1-phenyl-1-propyne (2), 3-phenyl-1-propyne (3), and phenylallene (4).

In this Letter, we present the first experimental evidence that the aromatic indene molecule together with its acyclic isomers can be formed via a ‘directed synthesis’ through the reaction of the phenyl radical with propyne and allene under combustion-relevant conditions (300 Torr, 1,200–1,500 K). Utilizing a high temperature ‘chemical reactor’, we synthesize the isomers *in situ* via reaction of pyrolytically¹⁰ generated phenyl radicals (C_6H_5) with two C_3H_4 isomers - allene (H_2CCCH_2) and propyne (CH_3CCH) - followed by isomerization and/or fragmentation of the initial C_9H_9 collision complexes. Note that for distinct structural isomers, the adiabatic ionization energy (IE) and the corresponding photoionization efficiency (PIE) curves, which report the ion signal of $m/z = 116$ ($C_9H_8^+$) of a distinct isomer versus the photon energy, can differ dramatically.^{11,12} By photoionizing the neutral C_9H_8 products in the supersonic molecular beam via tunable vacuum ultraviolet (VUV) radiation from the Advanced Light Source at various photon energies, we measured PIEs of $m/z = 116$ ($C_9H_8^+$) in the propyne (PIE_{MA}) and

allene (PIE_{AL}) experiments. These PIE curves are the result of a linear combination of PIE curves of the individual C₉H₈ isomers present in the supersonic beams and hence we can identify the C₉H₈ products formed in the reactions of phenyl radicals with propyne and allene, and establish their branching ratios.

The mass spectra of the species formed in the supersonic expansion and the PIE curves of $m/z = 116$ (C₉H₈⁺) recorded in the propyne (PIE_{MA}) and allene (PIE_{AL}) experiments are compiled in Figures 2 and in Figure 3, respectively. Figure 3 depicts data over a range of photon energies from 7.9 to 8.5 eV together with the PIE curves of the individual C₉H₈ isomers (1)-(4) (Figure 1) (unpublished results). The PIE curves for the allene (upper) and propyne (center) system differ strongly with PIE_{AL} showing an intense onset of the ion signal at about 8.1 eV compared to a shallow increase at 8.1 eV for PIE_{MA}. Among all C₉H₈ isomers, the indene molecule (1) depicts the lowest ionization energy (IE) of 8.15 ± 0.05 eV,¹³ which correlates nicely with the onset of the rise of both PIE curves. A detailed analysis of the PIE curves suggests that in case of the phenyl – allene system, indene represents the dominating C₉H₈ isomer formed with 71 ± 10 % followed by phenylallene and 3-phenyl-1-propyne (Table 1). These branching ratios are distinctively different from those derived for the phenyl – propyne system. Here, indene and phenylallene are relatively minor products with the 1-phenyl-1-propyne isomer being the dominant product formed. In an attempt to rationalize the formation of the indene molecule together with the distinct branching ratios of the isomers formed in both systems, we took a closer look at the underlying potential energy surfaces (PESs). Figure 4 compiles the relevant sections of the potential energy surfaces for the reactions of the phenyl radical with propyne and allene leading to four C₉H₈ isomers. All optimized structures were taken from density functional calculations in the previous works,⁶⁻⁸ but their relative energies were refined here using a chemically accurate G3-type computational scheme.

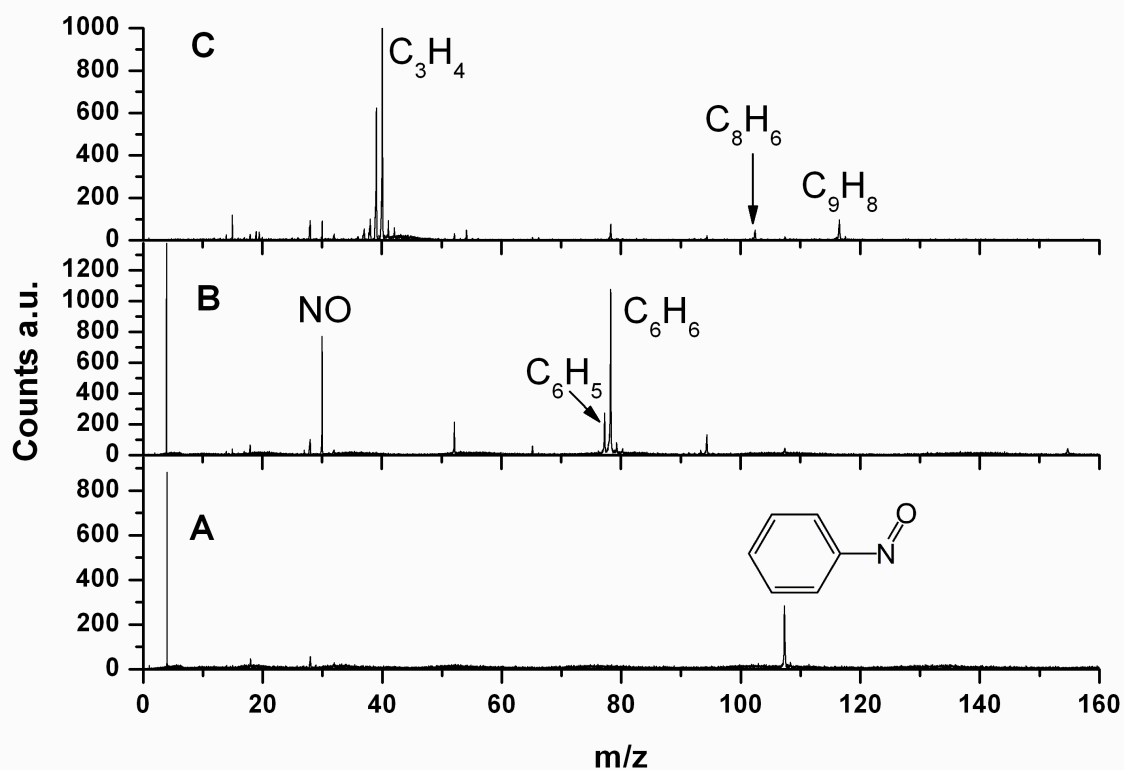


Figure 2: Mass spectra of prominent species in the helium-seeded supersonic nitrosobenzene beam without heating the nozzle [nitrosobenzene (C_6H_5NO)] (A), with heating the nozzle [nitrogen monoxide (NO); phenyl radical (C_6H_5); benzene (C_6H_6)] (B), and in the heated nitroso benzene beam entrained in propyne [propyne (C_3H_4); phenylacetylene (C_8H_6); C_9H_8 isomers] (C) recorded at a photon energy of 10 eV.

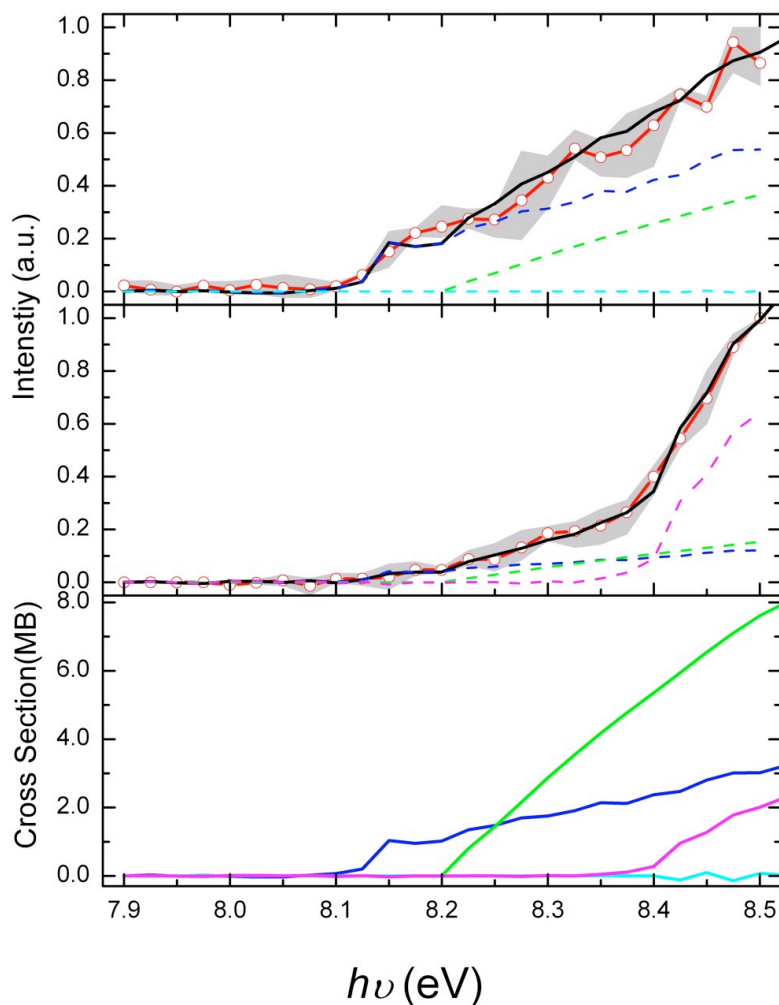


Figure 3: Upper panel: Red circles and line are the PIE data obtained in the phenyl – allene system at $m/z = 116$. The black line presents the cumulative simulated PIE from the individual PIE curves of indene (1) (blue), phenylallene (4) (green), and 3-phenyl-1-propyne (3) (cyan) with branching ratios listed in Table 1. Center panel: Red circles and line are the PIE data obtained in the phenyl – propyne system at $m/z = 116$. The black line presents the cumulative simulated PIE from the individual PIE curves of indene (1) (blue), phenylallene (4) (green), and 1-phenyl-1-propyne (magenta) with branching ratios listed in Table 1. Lower panel: individual PIE curves of four C_9H_8 isomers: indene (1) (blue), phenylallene (4) (green), 1-phenyl-1-propyne (2) (magenta), and 3-phenyl-1-propyne (3) (cyan). The shaded area present the 1σ error limits as derived from averaging four scans from 7.9 to 8.5 eV.

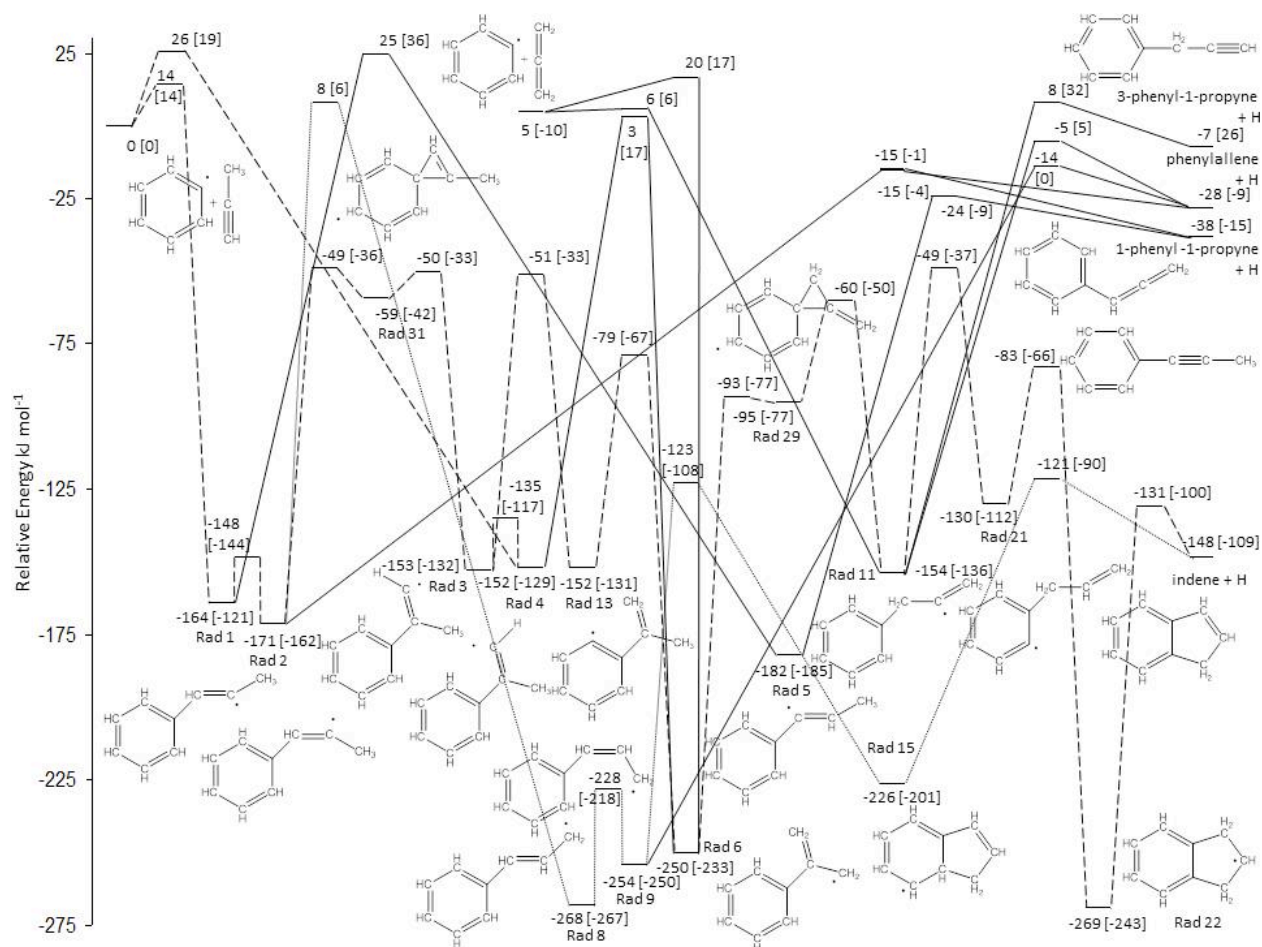


Figure 4: Relevant sections of the C_9H_9 potential energy surface (PES) accessed in the reactions of the phenyl radical with allene and propyne leading to four C_9H_8 isomers. All relative energies (in kJ mol^{-1}) were calculated at the G3(MP2,CC)//B3LYP/6-311+G** + ZPE(B3LYP/6-311+G**) level of theory. The labels of the reaction intermediates *Rad* and the energetics in square brackets were taken from References 6-8.

Table 1: Branching ratios of distinct C_9H_8 isomers formed in the phenyl – allene and phenyl – propyne systems utilizing a chemical reactor at 300 Torr and 1,200 – 1,500 K.

reactant	indene	phenylallene	1-phenyl-1-propyne	3-phenyl-1-propyne
allene	$71 \pm 10 \%$	$19 \pm 5 \%$	0	$< 10 \pm 5 \%$
propyne	$10 \pm 5 \%$	$8 \pm 5 \%$	$82 \pm 10 \%$	0

Considering the phenyl – propyne system, electronic structure calculations⁶⁻⁸ suggest that the phenyl radical adds with its radical center to the sterically less-hindered C1-position of the propyne molecule forming a reaction intermediate *Rad 1*, which undergoes a rapid cis-trans isomerization to *Rad 2*. The latter can emit a hydrogen atom either from the acetylenic carbon atom or from the methyl group of the propyne moiety leading to the formation of 1-phenyl-1-propyne and phenylallene, respectively, via tight transition states. The energetically least favorable isomer, the 3-phenyl-1-propyne molecule, cannot be accessed via the decomposition of *Rad 2*. The indene molecule can only be synthesized via a complex series of isomerization steps from *Rad 2* involving eight intermediates along the dashed line. The isomerization sequence *Rad 8* → *Rad 9* → *Rad 15* as depicted in the dotted line presents an alternative pathway to form indene plus atomic hydrogen. A comparison of these theoretically feasible pathways with the experimental data suggests the following scenario. In the chemical reactor, the phenyl radical adds to the C1-carbon atom of propyne forming *Rad 1* which isomerizes to *Rad 2*. The life time of the majority of the *Rad 2* intermediates is likely quite short so that a predominant fraction of *Rad 2* decomposes to 1-phenyl-1-propyne, i.e. via hydrogen emission from the C1 carbon atom; here, the energy randomization in *Rad 2* is incomplete thus significantly inhibiting an ‘energy flow’ across the carbon-carbon skeleton to the carbon-hydrogen bonds of the methyl group; this in turn would reduce the formation of phenylallene compared to 1-phenyl-1-propyne as observed experimentally. However, keeping in mind that the experiments are not conducted under single collision conditions (multiple collisions can deactivate the reaction intermediates thus increasing their life time), the experimental data suggests that a smaller fraction of the intermediates *Rad 2* form the indene molecule involving multiple isomerization steps; considering the heights of the barriers to access *Rad 31* (dashed route) and *Rad 8* (dotted route), the formation of the indene molecule should proceed preferentially via the dashed line. This conclusion is in line with previous computations.⁶⁻⁸

In case of the phenyl – allene system, the calculations predict an addition of the phenyl radical with its radical center to the C1 or C2 (central) carbon atom of the allene molecule leading to intermediates *Rad 11* and *Rad 6*, respectively. *Rad 11* could eliminate a hydrogen atom from the C1 or C3 carbon atom of the allene moiety forming either phenylallene or 3-phenyl-1-propyne. Note that similar to the phenyl – propyne system, if the energy randomization of the majority of *Rad 11* is incomplete thus largely inhibiting an effective energy transfer to the terminal CH₂

group, phenylallene should be formed preferentially compared to 3-phenyl-1-propyne. This was clearly observed experimentally. The major difference in the reactions of phenyl with propyne and allene presents the significantly increased fraction of indene formation in the allene reaction. A closer look at the relevant part of the PES might explain this finding. Upon formation of *Rad 11*, only two isomerization steps to *Rad 22* are necessary prior to the decomposition to the indene molecule; four steps are necessary if *Rad 6* is formed initially. On the other hand, the formation of indene in the phenyl – propyne system involves eight reaction steps, among them the common intermediate *Rad 11*. Therefore, the experimental results and the computations suggest that *Rad 11* likely presents a common intermediate in the formation of indene molecule in the reactions of the phenyl radical with both propyne and allene. Considering that only two additional reaction steps are involved in the indene synthesis in the phenyl – allene system, but eight in the phenyl – propyne reaction, indene is preferentially formed in the reaction of phenyl radicals with allene as verified experimentally (Table 1).

To summarize, our experiments utilizing a high temperature chemical reactor established for the first time that the aromatic indene molecule can be synthesized under combustion-like conditions via a *directed* synthesis through the reactions of the phenyl radical with allene and propyne, with the allene system giving seven times higher yields. Therefore, these pathways may also account for the synthesis of indene in ‘real’ hydrocarbon flames.¹⁴⁻¹⁹ Besides the PAH indene, we also detected three acyclic isomers - phenylallene and 3-phenyl-1-propyne (allene system) and phenylallene and 1-phenyl-1-propyne (propyne system) and proposed their formation routes. We believe that this thermal chemical reactor will be a convenient source for ‘directed’ synthesis of more complex PAHs via reactions with C3 and C4 hydrocarbons under controlled conditions in future experiments.

EXPERIMENTAL & THEORETICAL METHODS

The centerpiece of the experiments is a resistively heated high temperature ‘chemical reactor’ incorporated into the molecular beams end station²⁰ at the Chemical Dynamics Beamline (9.0.2.) of the Advanced Light Source. This reactor allows an experimental simulation of combustion-relevant conditions (temperatures, pressures) and chemical reactions to form PAHs and their acyclic isomers *in situ*. Briefly, a continuous beam of phenyl radicals (C_6H_5) was generated *in situ* via quantitative pyrolysis¹⁰ of nitrosobenzene (C_6H_5NO ; Aldrich) - held at 293 K - seeded

in the hydrocarbon carrier gas (allene [H_2CCCH_2 ; 97 %; Sigma] or propyne [CH_3CCH ; 98 %; Sigma]) expanded at a backing pressure of 300 Torr through a 0.1 mm orifice into a resistively heated silicon carbide (SiC) tube. In the present experiments, a heating current of 1.3 A was applied to the silicon carbide tube resulting in an operating power of 20 W. An external temperature calibration of the pyrolytic source with pure helium carrier gas coupled to a time-of-flight mass spectrometer and chopper wheel suggested temperatures of 1,200 – 1,500 K of the silicon carbide tube. Note that the hydrocarbon did not only act as a seeding gas, but also as a reactant with the pyrolytically generated phenyl radicals. This machine provides an unprecedented tool to analyze these *in situ* generated PAHs and their isomers. Here, after passing a 2 mm skimmer located 10 mm downstream from the silicon carbide nozzle, quasi continuous tunable vacuum ultraviolet (VUV) radiation from the Advanced Light Source crossed the neutral molecular beam at the extraction region of a Wiley–McLaren Reflectron Time-of-Flight (Re-TOF) mass spectrometer 55 mm downstream. *Fragment-free* VUV photoionization mass spectrometry – a *soft ionization method* - is unmatched by traditional ionization techniques utilizing electron impact schemes.²¹ The ions of the photoionized molecules were then extracted and collected by a microchannel plate detector in the Re-TOF mode utilizing a multi channel scaler. The photoionization efficiency (PIE) curves were obtained by plotting the integrated relevant ion counts at a desired mass-to-charge, m/z , versus the photoionization energy between 7.900 eV and 8.600 eV in steps of 0.025 eV. The signal was normalized to the photon flux. Based on known PIE curves of expected PAHs of a well-defined molecular mass and their acyclic isomers ($m/z = 116$; C_9H_8), the recorded PIE curves were then fit via a linear combination with known PIE curves of various C_9H_8 isomers to extract the nature of the products formed and their branching ratios.

In our theoretical calculations of the potential energy surfaces, we utilized geometries of various species from the previous works⁹⁻¹¹ optimized at the B3LYP/6-311+G** level of theory. To obtain more accurate energies, we applied the G3(MP2,CC)//B3LYP modification^{22,23} of the original Gaussian 3 (G3) scheme²⁴ for high-level single-point energy calculations. The final energies at 0 K were obtained using the B3LYP optimized geometries and ZPE corrections according to the following formula (1)

$$(1) \quad E_0[\text{G3}(\text{MP2,CC})] = E[\text{CCSD}(\text{T})/6-311\text{G}(\text{d,p})] + \Delta E_{\text{MP2}} + E(\text{ZPE}),$$

where $\Delta E_{\text{MP2}} = E[\text{MP2/G3large}] - E[\text{MP2/6-311G(d,p)}]$ is the basis set correction and $E(\text{ZPE})$ is the zero-point energy. $\Delta E(\text{SO})$, a spin-orbit correction, and $\Delta E(\text{HLC})$, a higher level correction, from the original G3 scheme were not included in our calculations, as they are not expected to make significant contributions into relative energies. We used the Gaussian 98²⁵ program package to carry out MP2 calculations, and the Molpro 2002²⁶ program package to perform calculations of spin-restricted coupled cluster RCCSD(T) energies.

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REFERENCES

- (1) Kazakov, A.; Frenklach, M. On the relative contribution of acetylene and aromatics to soot particle surface growth *Combust. Flame* **1998**, *112*, 270-274.
- (2) Frenklach, M. Reaction mechanism of soot formation in flames *Phys. Chem. Chem. Phys.* **2002**, *4*, 2028-2037.
- (3) Frenklach, M.; Feigelson, E. D. Formation of polycyclic aromatic hydrocarbons in circumstellar envelopes *Astrophys. J.* **1989**, *341*, 372-384.
- (4) Unterreiner, B. V.; Sierka, M.; Ahlrichs, R. Reaction pathways for growth of polycyclic aromatic hydrocarbons under combustion conditions, a DFT study *Phys. Chem. Chem. Phys.* **2004**, *6*, 4377-4384.
- (5) Fascella, S.; Cavallotti, C.; Rota, R.; Carra, S. Quantum Chemistry Investigation of Key Reactions Involved in the Formation of Naphthalene and Indene *J. Phys. Chem. A* **2004**, *108*, 3829-3843.
- (6) Vereecken, L.; Bettinger, H. F.; Peeters, J. Reactions of chemically activated C₉H₉ species. Part I. The product distribution of the reaction of phenyl radicals with propyne *Phys. Chem. Chem. Phys.* **2002**, *4*, 2019-2027.
- (7) Vereecken, L.; Peeters, J. Reactions of chemically activated C₉H₉ species II: The reaction of phenyl radicals with allene and cyclopropene, and of benzyl radicals with acetylene *Phys. Chem. Chem. Phys.* **2003**, *5*, 2807-2817.
- (8) Vereecken, L.; Peeters, J.; Bettinger, H. F.; Kaiser, R. I.; Schleyer, P. v. R.; Schaefer, H. F., III. Reaction of Phenyl Radicals with Propyne *J. Am. Chem. Soc.* **2002**, *124*, 2781-2789.
- (9) Kaiser, R. I.; Balucani, N. The formation of nitriles in hydrocarbon-rich atmospheres of planets and their satellites: laboratory investigations by the crossed molecular beam technique *Acc. Chem. Res.* **2001**, *34*, 699-706.
- (10) Kohn, D. W.; Clauberg, H.; Chen, P. Flash pyrolysis nozzle for generation of radicals in a supersonic jet expansion *Rev. Sci. Instrum.* **1992**, *63*, 4003-4005.
- (11) Kaiser, R. I.; Belau, L.; Leone, S. R.; Ahmed, M.; Wang, Y.; Braams, B. J.; Bowman, J. M. A combined experimental and computational study on the ionization energies of the cyclic and linear C₃H isomers *Chem Phys Chem* **2007**, *8*, 1236-1239.
- (12) Kaiser, R. I.; Mebel, A.; Kostko, O.; Ahmed, M. On the ionization energies of C₄H₃ isomers *Chem. Phys. Lett.* **2010**, *485*, 281-285.
- (13) Gusten, H.; Klasinc, L.; Ruscic, B., Photoelectron spectroscopy of J. Heterocycl. Chem.. Indene analogs, *Z. Naturforsch. A.*, **1976**, *31*, 1051.
- (14) Kamphus, M.; Braun-Unkhoff, M.; Kohse-Hoeinghaus, K. Formation of small PAHs in laminar premixed low-pressure propene and cyclopentene flames: Experiment and modeling *Combust. Flame* **2008**, *152*, 28-59.
- (15) Li, Y.; Zhang, L.; Tian, Z.; Yuan, T.; Zhang, K.; Yang, B.; Qi, F. Investigation of the rich premixed laminar acetylene/oxygen/argon flame: comprehensive flame structure and special concerns of polyynes *Proc. Combust. Inst.* **2009**, *32*, 1293-1300.
- (16) Li, Y.; Zhang, L.; Yuan, T.; Zhang, K.; Yang, J.; Yang, B.; Qi, F.; Law, C. K. Investigation on fuel-rich premixed flames of monocyclic aromatic hydrocarbons: Part I. Intermediate identification and mass spectrometric analysis *Combust. Flame* **2010**, *157*, 143-154.
- (17) Li, Y.; Zhang, L.; Tian, Z.; Yuan, T.; Wang, J.; Yang, B.; Qi, F. Experimental Study of a Fuel-Rich Premixed Toluene Flame at Low Pressure *Energy & Fuels* **2009**, *23*, 1473-1485.

- (18) Li, Y.; Cai, J.; Zhang, L.; Yuan, T.; Zhang, K.; Qi, F. Investigation on chemical structures of premixed toluene flames at low pressure *Proc. Combust. Inst.* **2011**, *33*, 593-600.
- (19) Li, Y.; Cai, J.; Zhang, L.; Yang, J.; Zhang, K.; Qi, F. Experimental and modeling investigation on premixed ethylbenzene flames at low pressure *Proc. Combust. Inst.* **2011**, *33*, 617-624.
- (20) Nicolas, C.; Shu, J.; Peterka, D. S.; Hochlaf, M.; Poisson, L.; Leone, S. R.; Ahmed, M. Vacuum Ultraviolet Photoionization of C₃ *J. Am. Chem. Soc.* **2006**, *128*, 220-226.
- (21) Hanley, L.; Zimmermann, R. Light and Molecular Ions: The Emergence of Vacuum UV Single-Photon Ionization in MS *Anal. Chem. (Washington, DC, U. S.)* **2009**, *81*, 4174-4182.
- (22) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650-7657.
- (23) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Baboul, A. G.; Pople, J. A. *Chem. Phys. Lett.* **1999**, *314*, 101-107.
- (24) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764-7776.
- (25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C. et al. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.
- (26) MOLPRO, a package of *ab initio* programs designed by Werner, H.-J. and Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C. et al. version 2002.1.

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