TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2023 SUMMER SCHOOL ON COMBUSTION

Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

Nils Hansen
Sandia National Laboratories
July 12−14, 2023

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GAS PHASE CHEMICAL PHYSICS

Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

Nils Hansen

Sandia National Laboratories

COMBUSTION RESEARCH FACILITY
CRF
SANDIA NATIONAL LABORATORIES / CALIFORNIA

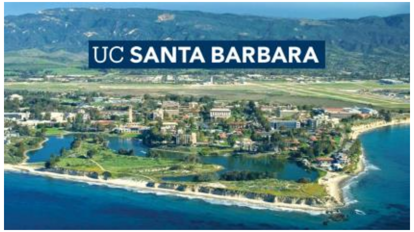
Introduction

Name:	Nils Hansen
Education:	Diploma-Degree in Chemistry, Christian-Albrechts-Universität Kiel
	PhD (Dr. rer. nat.) in Physical Chemistry at the Christian-Albrechts-Universität Kiel, Germany
Professional Career:	Postdoc at the University of California Santa Barbara, USA
	Staff Scientist at the BASF AG, Ludswigshafen, Germany
	Staff Scientist at the Combustion Research Facility, Sandia National Laboratories
Research Interest:	Chemical kinetics of complex reaction networks

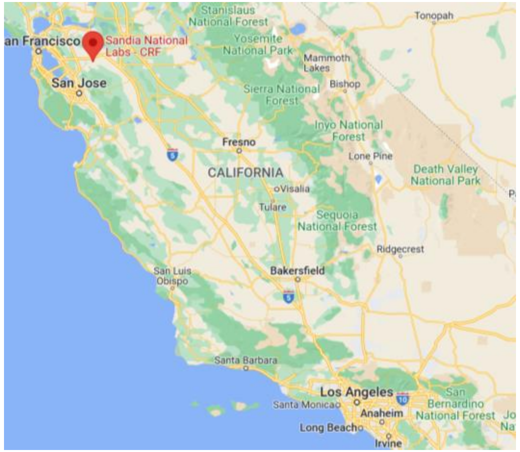
Sandia National Laboratories

C | A | U

Kiel University
Christian-Albrechts-Universität zu Kiel



BASF
We create chemistry



GAS PHASE CHEMICAL PHYSICS

Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

Lecture 1: Introduction

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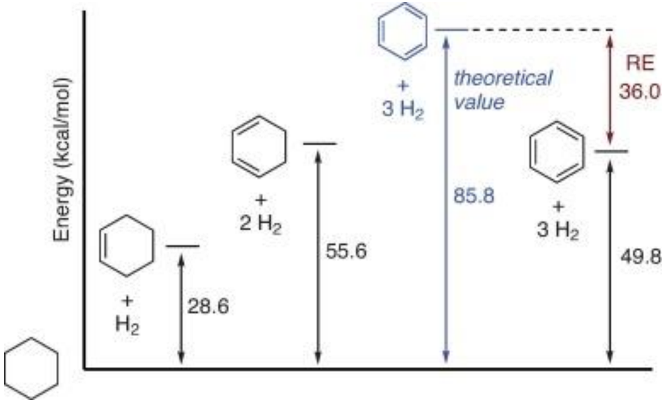
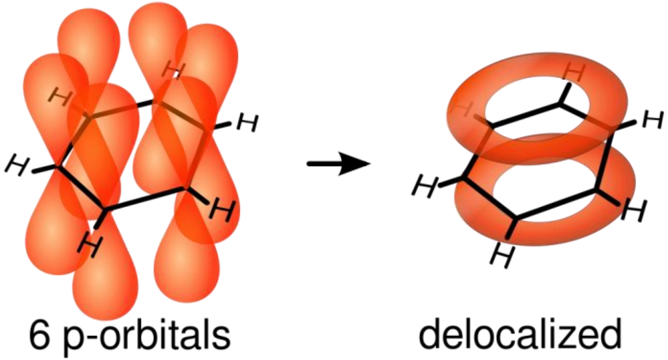
Aromaticity

- Unsaturated cyclic molecules that possess additional stabilization (Resonance Energy, RE) as a result of the arrangement of π-electrons associated with the unsaturation of the ring system.



C. S. López, O. N. Faza, "Overview of the computational methods to assess aromaticity" in "Aromaticity – Modern Computational Methods and Applications" (I. Fernandes, ed.), Elsevier, 2021

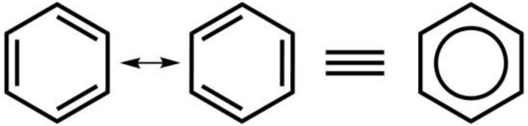


https://shiken.ai/chemistry/benzene-structure

Delocalized π-electron cloud (one above and one below the molecular plane).

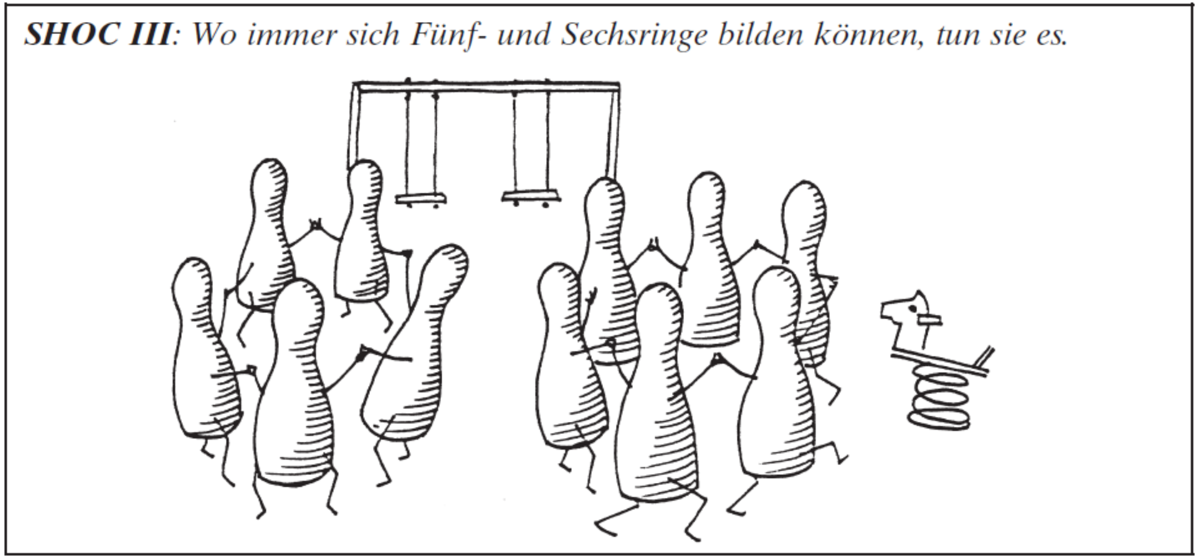
Hückel's Rule:

- ✓ A planar, cyclic system of unsaturated atoms containing ($4n$+2) π-electrons will be aromatic. n = 0, 1 (benzene), 2, …
- ✓ Slight deviation from planarity is allowed.



There are no localized C=C bonds.

Physical Organic Chemistry

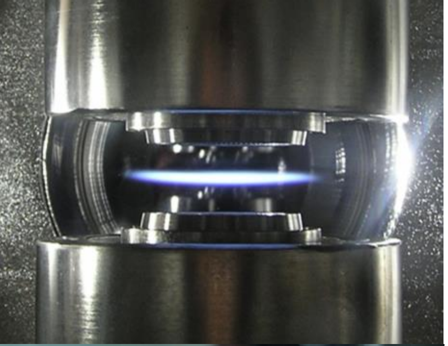


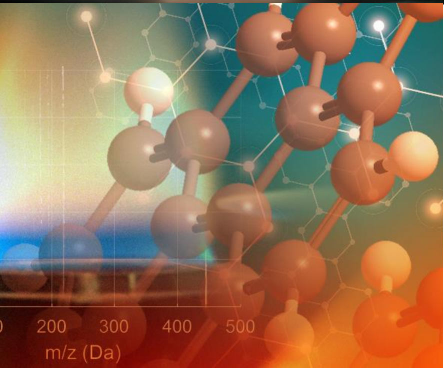
SHOC III: *Wo immer sich Fünf- und Sechsringe bilden können, tun sie es.*

U. Lüning, *Organische Reaktionen,* **2010,** Springer

Wherever five- and six-membered rings can form, they do it.

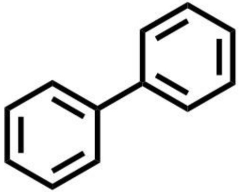
GAS PHASE CHEMICAL PHYSICS

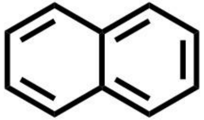


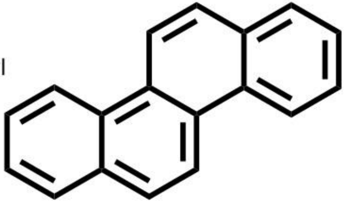


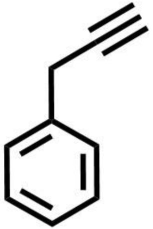
Polycyclic Aromatic Hydrocarbons (PAHs)

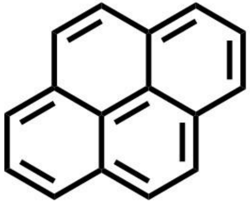
- PAHs are aromatic hydrocarbons which contain more than one benzene-like ring.
- One type of PAH contains two ore more benzene-like rings joined by a carbon-carbon single bond.
- Benzene rings may be fused to give larger polycyclic aromatics (one carbon-carbon bond is common to two aromatic rings)

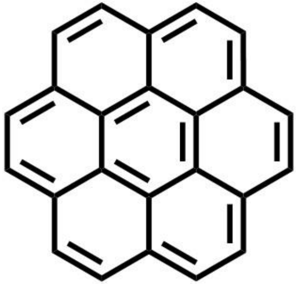

biphenyl

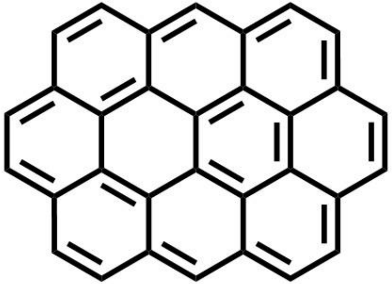

naphthalene


chrysene


phenylpropyne


pyrene

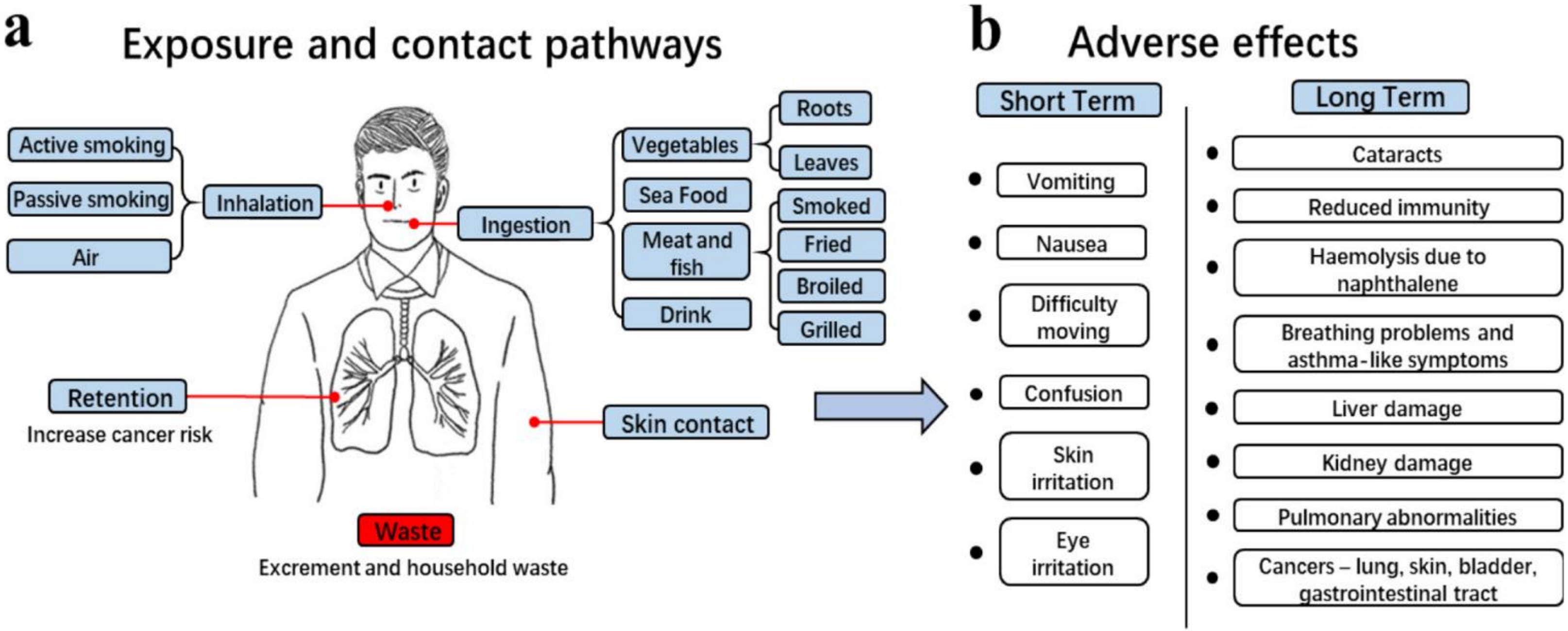

coronene


ovalene

GAS PHASE CHEMICAL PHYSICS

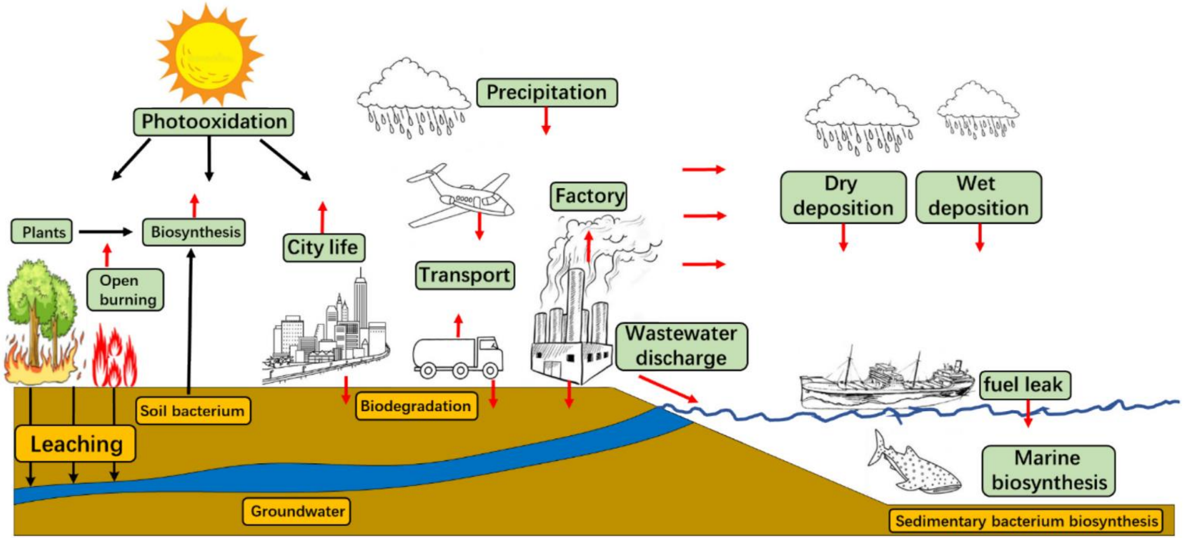
PAHs and the Environment

PAHs are a typical class of “three-causing” substances (carcinogenic, teratogenic and mutagenic)



K. Sun, Y. Song, F. He, M. Jing, J. Tang, R. Liu, A review of human and animals exposure to polycyclic aromatic hydrocarbons: Health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics, Science of the Total Environment 773 (2021) 145403

PAHs and the Environment



Main Natural Sources:

- ➢ combustion processes such as forest and prairie fires and volcanic eruptions

Main man-made sources:

- ➢ incomplete combustion of coal, petroleum, wood and organic polymer compounds
- ➢ leakage and discharge of crude oil, coal tar, asphalt, shale oil, carbon ink and various industrial mineral oils during the mining, transportation, production and use

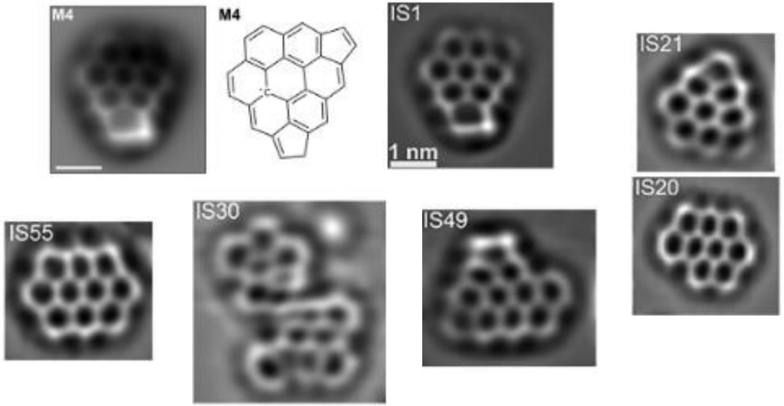
GAS PHASE CHEMICAL PHYSICS

K. Sun, Y. Song, F. He, M. Jing, J. Tang, R. Liu, A review of human and animals exposure to polycyclic aromatic hydrocarbons: Health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics, Science of the Total Environment 773 (2021) 145403

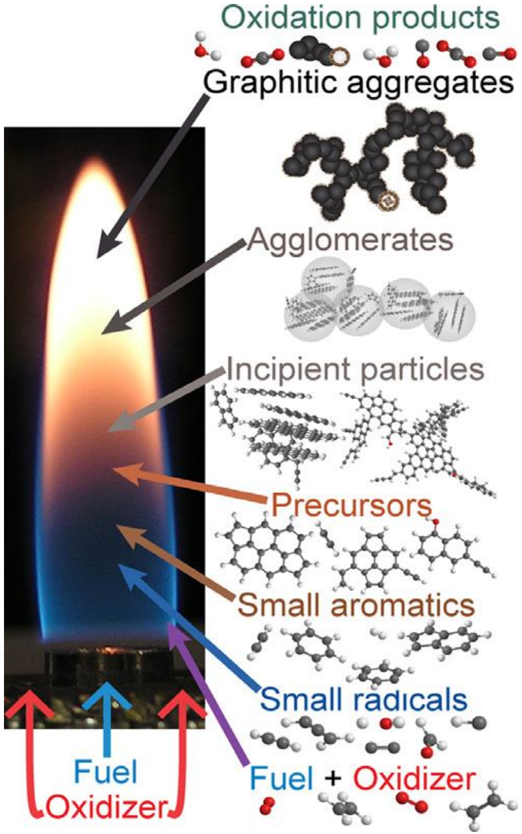
PAHs and Soot Formation

PAHs (incl. aliphatically bridged, and substituted PAHs) are considered soot precursors and candidates for precursors that drive soot inception.

High-Resolution Atomic Force Microscopy (AFM) Images:



F. Schulz *et al.*, *Proc. Combust. Inst.*, **2019,** 37, 885-892
M. Commodo *et al.*, *Combust. Flame.*, **2019,** 205, 154-164



H. A. Michelsen, *Proc. Combust. Inst.*, **2017,** 36(1), 717-735

Soot and the Environment

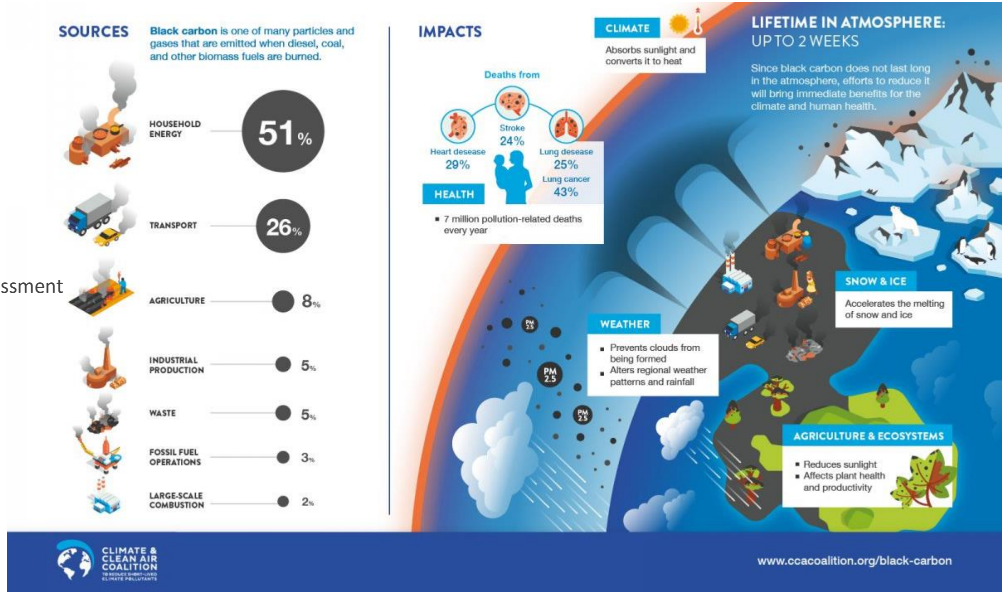
- ➢ Air pollution, especially airborne particulate matter (PM), is associated with an increase in both morbidity and mortality from cardiovascular disease

- ➢ Black carbon (BC) and correlated co-emissions appear causally related with all-cause, cardiovascular, and lung cancer mortality, and perhaps with adverse birth outcomes and central nervous system effects.

T. J. Grahame, “Public health and components of particulate matter: The changing assessment of black carbon”, *J. Air Waste Manage. Ass.,* **2014,** 64(6), 620-660, https://doi.org/10.1080/10962247.2014.912692

- ➢ components may be more important than PM concentration alone in explaining health responses

- ➢ linking composition to health impacts continues to accumulate in the epidemiological, toxicological, and controlled human exposure arenas



Black carbon is one of many particles and gases that are emitted when diesel, coal, and other biomass fuels are burned.

Absorbs sunlight and converts it to heat

- 7 million pollution-related deaths every year

Since black carbon does not last long in the atmosphere, efforts to reduce it will bring immediate benefits for the climate and human health.

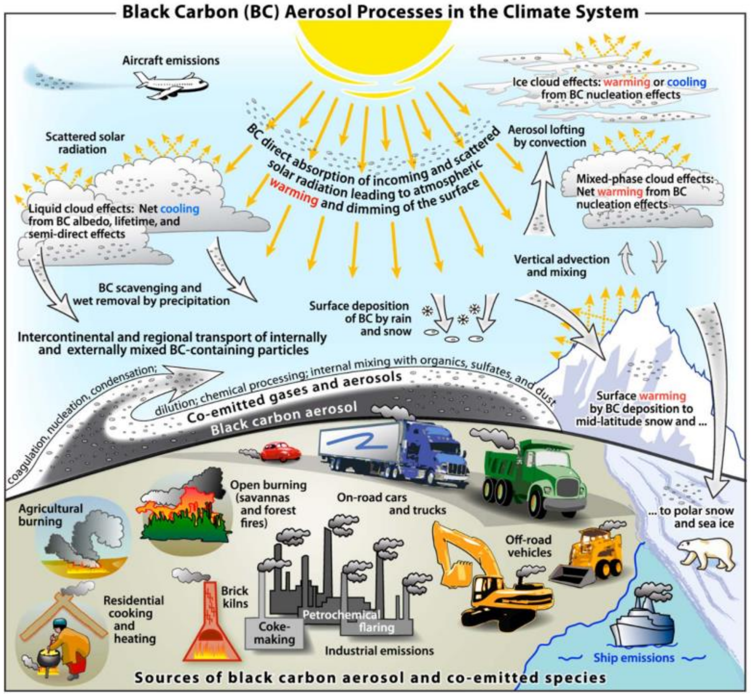
Accelerates the melting of snow and ice

- Prevents clouds from being formed
- Alters regional weather patterns and rainfall

- Reduces sunlight
- Affects plant health and productivity

Rohr and Wyzga, “Attributing health effects to individual particulate matter constituents”, *Atmos. Environ.,* **2012,** 62, 130-152

Soot and the Environment



- Black carbon (mature soot) is a distinct type of carbonaceous material that is formed primarily in flames and is directly emitted to the atmosphere
- The atmospheric lifetime of black carbon, its impact on clouds, and its optical properties depend on interactions with other aerosol components.
- Direct radiative forcing of black carbon is caused by absorption and scattering of sunlight.
- Black carbon influences the properties of ice clouds and liquid clouds through diverse and complex processes.
- Black carbon deposition on snow and ice causes positive climate forcing.
- The black-carbon climate forcings from the direct effect and snowpack changes cause the troposphere and the top of the cryosphere to warm, inducing further climate response in the form of cloud, circulation, surface temperature, and precipitation changes.

TC Bond *et al.*, *J. Geophys. Res.: Atmos.*, **2013,** 118, 5380-5552, doi:10.1002/jgrd.50171, 2013

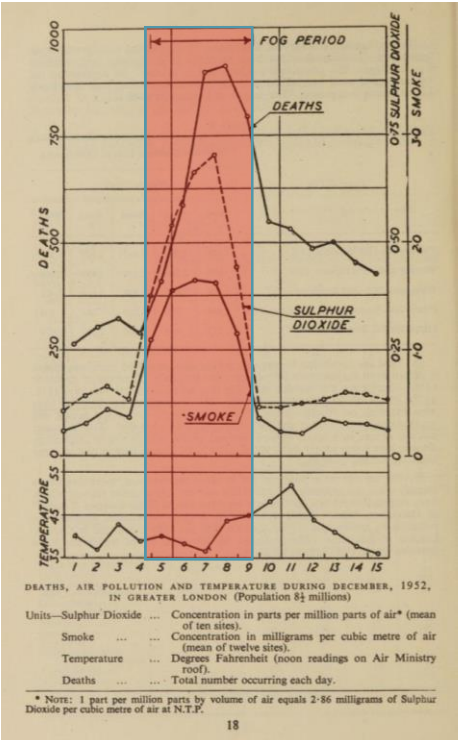
Soot and the Environment

London Smog of 1952 (Dec. 5th-9th)

Great Smog of London | 1952, Cause, Deaths, & Facts | Britannica

https://www.todayifoundout.com/index.php/2013/01/the-deadly-london-smog-of-1952/

- ➢ up to 4,000 people died as a direct result of the smog
- ➢ 100,000 more were made ill by the smog's effects on the human respiratory tract



DEATHS, AIR POLLUTION AND TEMPERATURE DURING DECEMBER, 1952, IN GREATER LONDON (Population $8\frac{1}{2}$ millions)

Units—Sulphur Dioxide ... Concentration in parts per million parts of air* (mean of ten sites).
Smoke ... ... Concentration in milligrams per cubic metre of air (mean of twelve sites).
Temperature ... Degrees Fahrenheit (noon readings on Air Ministry roof).
Deaths ... ... Total number occurring each day.

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* NOTE: 1 part per million parts by volume of air equals 2·86 milligrams of Sulphur Dioxide per cubic metre of air at N.T.P.

18

Beaver, Hugh (December 1953). "Great Britain Committee on Air Pollution: Interim Report". London: HMSO.

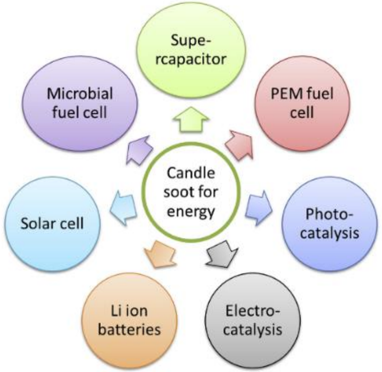
Useful Materials

Carbon black, representing a wide variety of engineered forms of mature soot, is used

- for automobile tires,
- as a pigment in toners for laser printers,
- for electronics/battery applications (incl. lithium ion batteries)

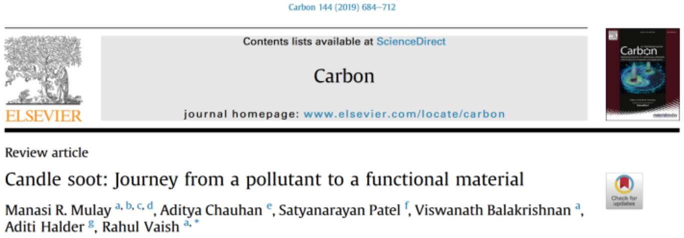
https://www.carbon-black.org/uses-of-carbon-black

Manet‘s “Music in the Tuileries”, 1862



Candle soot for energy

- Supe-rcapacitor
- PEM fuel cell
- Photo-catalysis
- Electro-catalysis
- Li ion batteries
- Solar cell
- Microbial fuel cell



Carbon 144 (2019) 684–712

Contents lists available at ScienceDirect

Carbon

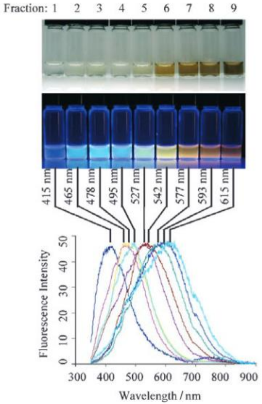
journal homepage: www.elsevier.com/locate/carbon

ELSEVIER

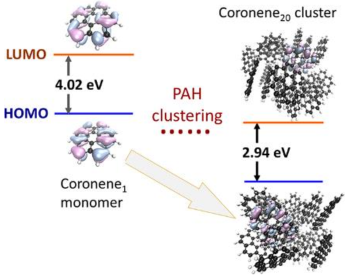
Review article

Candle soot: Journey from a pollutant to a functional material

Manasi R. Mulay [a, b, c, d], Aditya Chauhan [e], Satyanarayan Patel [f], Viswanath Balakrishnan [a], Aditi Halder [g], Rahul Vaish [a, *]



Chen and Wang, *J. Phys. Chem. C*, **2019,** 123, 27785–27793

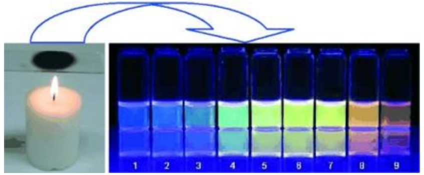


Fluorescent Nanoparticles

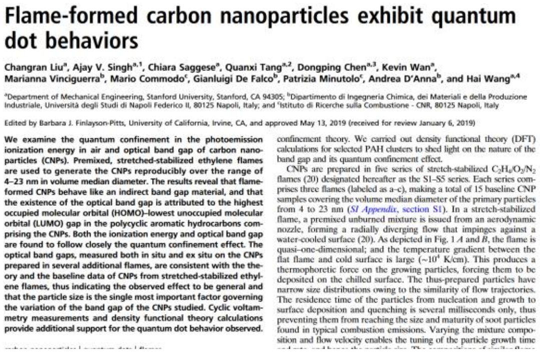
Fluorescent Carbon Nanoparticles Derived from Candle Soot**

*Haipeng Liu, Tao Ye, and Chengde Mao**

Liu *et al., Angew. Chem. Int. Ed.,* **2007,** 46(34), 6473-6475, https://doi.org/10.1002/anie.200701271



Useful Materials



Flame-formed carbon nanoparticles exhibit quantum dot behaviors

Changran Liu[a], Ajay V. Singh[a,1], Chiara Saggese[a], Quanxi Tang[a,2], Dongping Chen[a,3], Kevin Wan[a], Marianna Vinciguerra[b], Mario Commodo[c], Gianluigi De Falco[b], Patrizia Minutolo[c], Andrea D'Anna[b], and Hai Wang[a,4]

[a]Department of Mechanical Engineering, Stanford University, Stanford, CA 94305; [b]Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, 80125 Napoli, Italy; and [c]Istituto di Ricerche sulla Combustione - CNR, 80125 Napoli, Italy

Edited by Barbara J. Finlayson-Pitts, University of California, Irvine, CA, and approved May 13, 2019 (received for review January 6, 2019)

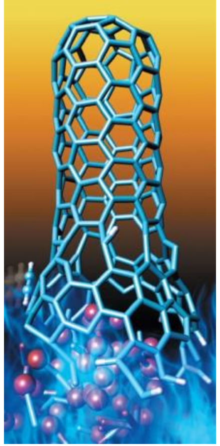
We examine the quantum confinement in the photoemission ionization energy in air and optical band gap of carbon nanoparticles (CNPs). Premixed, stretched-stabilized ethylene flames are used to generate the CNPs reproducibly over the range of 4–23 nm in volume median diameter. The results reveal that flame-formed CNPs behave like an indirect band gap material, and that the existence of the optical band gap is attributed to the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap in the polycyclic aromatic hydrocarbons comprising the CNPs. Both the ionization energy and optical band gap are found to follow closely the quantum confinement effect. The optical band gaps, measured both in situ and ex situ on the CNPs prepared in several additional flames, are consistent with the theory and the baseline data of CNPs from stretched-stabilized ethylene flames, thus indicating the observed effect to be general and that the particle size is the single most important factor governing the variation of the band gap of the CNPs studied. Cyclic voltammetry measurements and density functional theory calculations provide additional support for the quantum dot behavior observed.

confinement theory. We carried out density functional theory (DFT) calculations for selected PAH clusters to shed light on the nature of the band gap and its quantum confinement effect.

CNPs are prepared in five series of stretch-stabilized $C_2H_4/O_2/N_2$ flames (20) designated hereafter as the S1–S5 series. Each series comprises three flames (labeled as a–c), making a total of 15 baseline CNP samples covering the volume median diameter of the primary particles from 4 to 23 nm (*SI Appendix*, section S1). In a stretch-stabilized flame, a premixed unburned mixture is issued from an aerodynamic nozzle, forming a radially diverging flow that impinges against a water-cooled surface (20). As depicted in Fig. 1 *A* and *B*, the flame is quasi–one-dimensional; and the temperature gradient between the flat flame and cold surface is large ($\sim 10^4$ K/cm). This produces a thermophoretic force on the growing particles, forcing them to be deposited on the chilled surface. The thus-prepared particles have narrow size distributions owing to the similarity of flow trajectories. The residence time of the particles from nucleation and growth to surface deposition and quenching is several milliseconds only, thus preventing them from reaching the size and maturity of soot particles found in typical combustion emissions. Varying the mixture composition and flow velocity enables the tuning of the particle growth time

semiconducting particles of a few nanometres in size, that have optical and electronic properties that differ from those of larger particles as a result of quantum mechanics

Liu *et al., Proc. Nat. Acad. Sci.,* **2019,** 116(26), 12692-12697, https://doi.org/10.1073/pnas.1900205116



Carbon nanotubes grow in combustion flames

by Ayako Miyazaki, Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya
https://phys.org/news/2014-04-carbon-nanotubes-combustion-flames.html

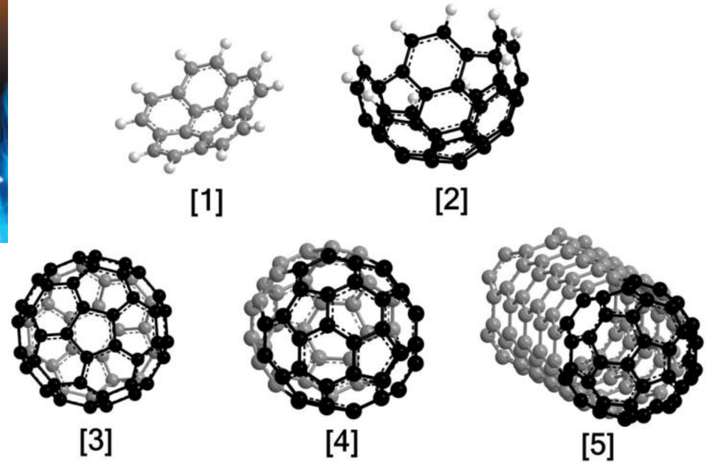
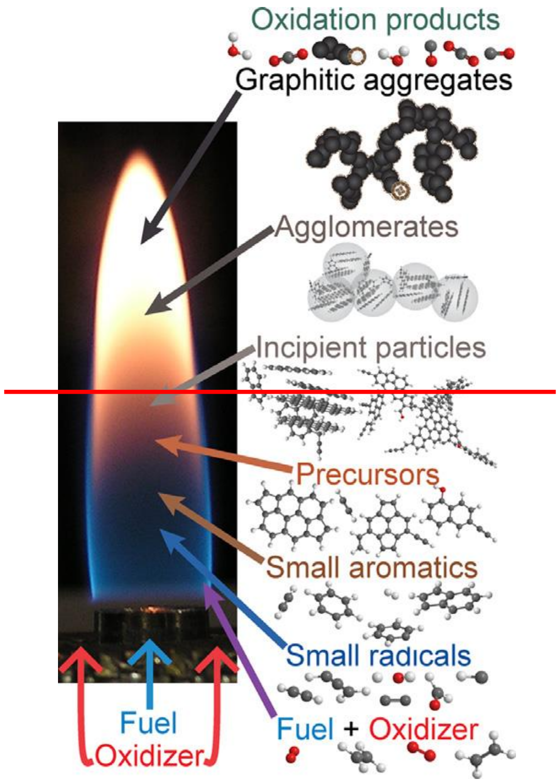


Fig. 1 | Molecular structures of 3-dimensional carbonaceous nanostructures. The smallest nanobowl, corannulene [1], as well as the C40 nanobowl [2] emphasized as a molecular building block of Buckminsterfullerene (C_{60}) [3], rugbyballene (C_{70}) [4], and end-capped (5,5) armchair nanotubes [5]. The C40 nanobowl carbons are black, the remaining carbons are gray, and the hydrogens are white.

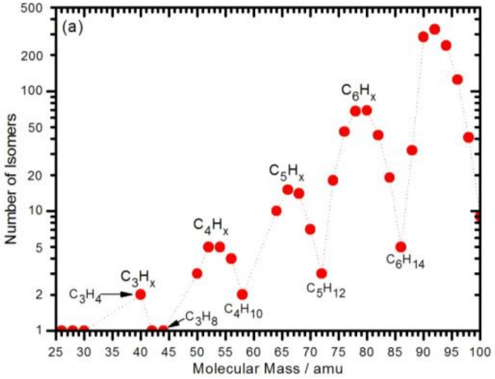
Gas phase synthesis of the C_{40} nano bowl $C_{40}H_{10}$
L. B. Tuli et al. *Nat Commun* **14**, 1527 (2023). https://doi.org/10.1038/s41467-023-37058-y

Molecular-Weight Growth and Soot Formation



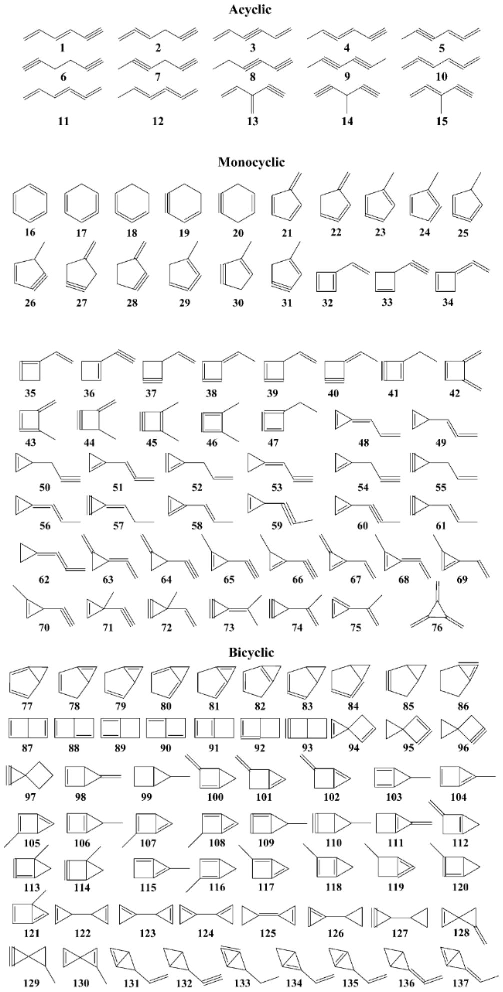
H. A. Michelsen, *Proc. Combust. Inst.*, **2017,** 36(1), 717-735

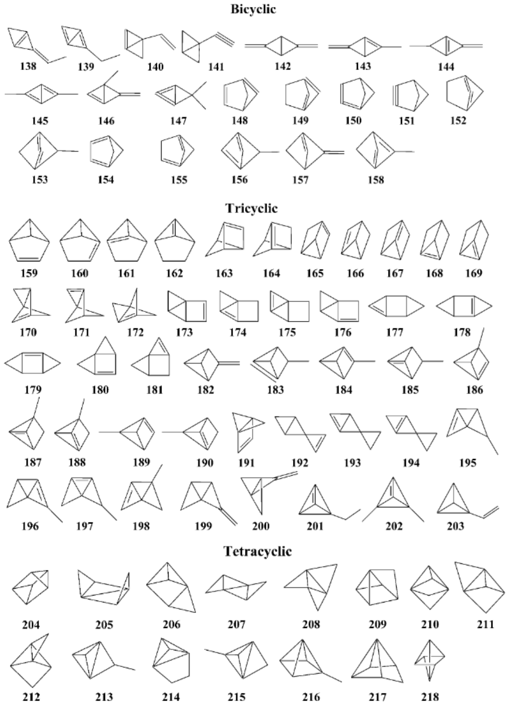
- extremely high number of molecules/isomers
- different chemical families (with different functional groups, …, different C/H ratios) to be present
- identification of key intermediates
- determining accurate spatially (or timely) resolved concentrations (uncertainties …)
- interpretation of the data
- reconciliation of measurements and mechanisms
- clogging of sampling probes
- modeling of idealized experiments (flames) and not real experiments (probe effects)



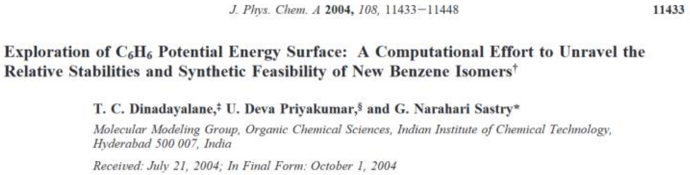
N. Hansen *et al.*, *Prog. Energy Combust. Sci.*, **2009,** 35(2), 168-191

C_6H_6 Isomers





[a] The triple bond and the allenic part outside the ring and in acyclic isomers are shown bent for convenience in drawing.


J. Phys. Chem. A **2004,** *108,* 11433−11448 11433

Exploration of C_6H_6 Potential Energy Surface: A Computational Effort to Unravel the Relative Stabilities and Synthetic Feasibility of New Benzene Isomers[†]

T. C. Dinadayalane,[‡] U. Deva Priyakumar,[§] and G. Narahari Sastry*

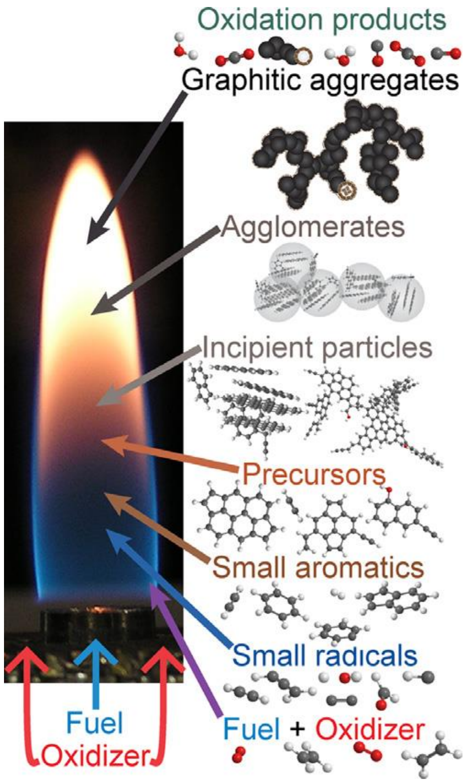
Molecular Modeling Group, Organic Chemical Sciences, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received: July 21, 2004; In Final Form: October 1, 2004

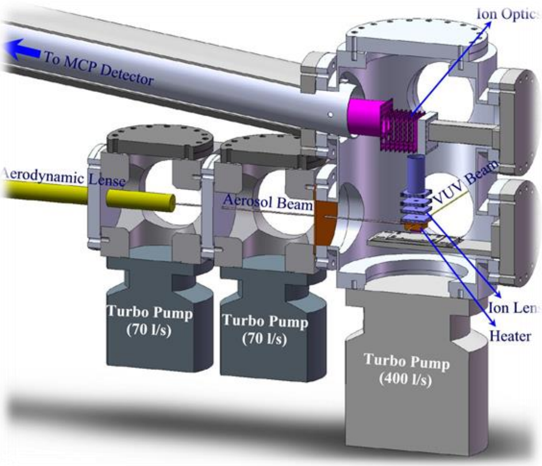
Established Experiments

Mass Spectrometry with soft-Ionization via synchrotron-generated vacuum-ultraviolet radiation

Advanced Light Source, Berkeley (USA), National Synchrotron Radiation Laboratory, USTC Hefei (China), Swiss Light Source, PSI (Switzerland), Soleil, ...



H. A. Michelsen, *Proc. Combust. Inst.*, **2017,** 36(1), 717-735



Flow Reactor

F. Qi + Y. Li (Shanghai), Z. Wang (USTC), B. Yang (Tsinghua), et al. + users (Bielefeld, KAUST, etc.)

Near Threshold Aerosol Mass Spectrometry

H. Michelsen (Sandia, CU Boulder)

Flames (premixed, counter- and coflow)

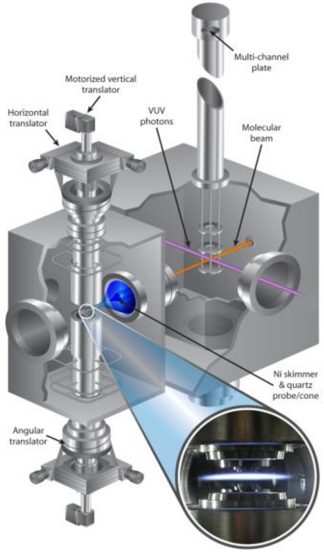
K. Kohse-Höinghaus, T. Kasper, N. Hansen, P.R. Westmoreland, F. Qi, Y. Li, et al.

High-Rep rate-Miniature Shocktube

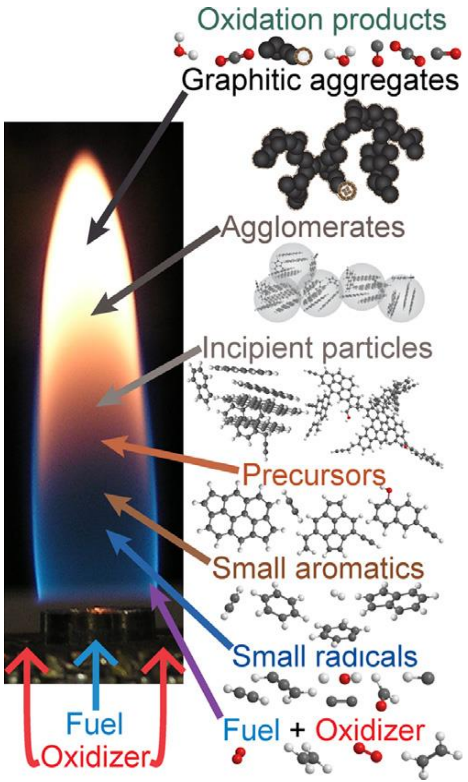
R. S. Tranter (Argonne), P. Lynch (UI)

Microtubular Reactor (Chen nozzle)

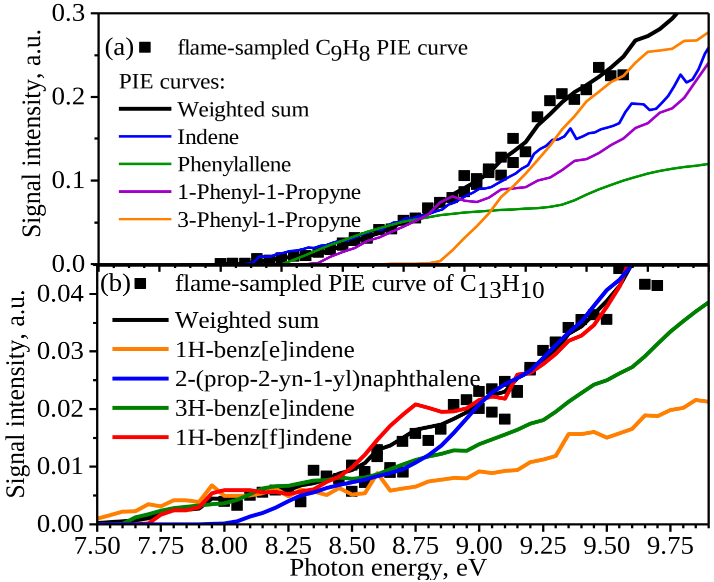
R. I. Kaiser (Hawaii), N. J. Labbe/B. Ellison (CU Boulder), N. Hansen



Experimental Challenges



H. A. Michelsen, *Proc. Combust. Inst.*, **2017,** 36(1), 717-735



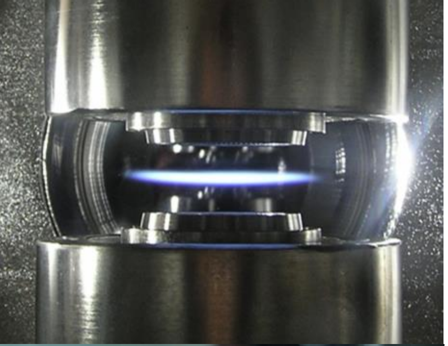
G. Kukkadapu, S. W. Wagnon, W. J. Pitz, N. Hansen, *Proc. Combust. Inst.*, **2021,** 38(1), 1477-1485

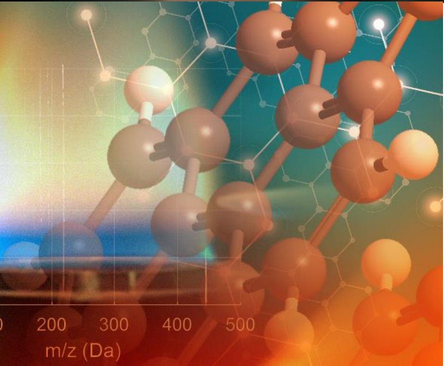
- Smaller differences in heats of formation and similar structural features result in almost identical IE‘s and indistinguishable PIE curves for larger species
- IE‘s and PIE curves may not be known and need to be measured/calculated

Outline of this Course:

1. Overview and Introduction
2. Formation of Benzene (C_3H_3 + C_3H_3, C_3H_3 + C_3H_5, *i*-C_4H_5 + C_2H_2, …)
3. Hydrogen-Abstraction-C_2H_2-Addition (HACA)
4. Formation of Naphthalene
5. Formation of Indene
6. Ring-Enlargement and other Reactions
7. Repetitive Pathways

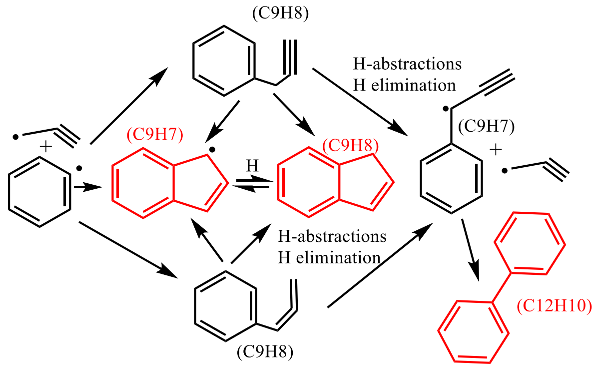
8.+9. Particle Inception

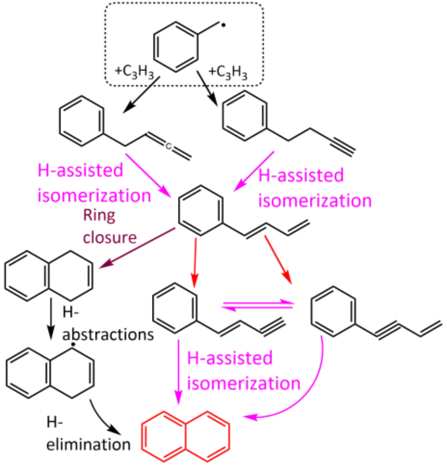


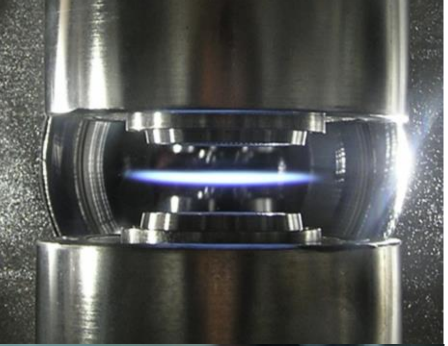


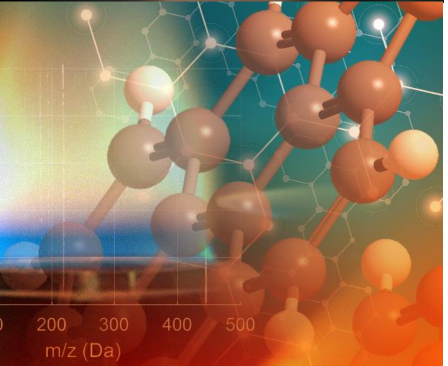
Goals:

1. **To provide an overview of chemical pathways leading to polycyclic aromatic hydrocarbons (PAHs)**
2. **To develop chemical understanding on how PAHs are formed in combustion environments**









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Progress in Energy and Combustion Science, 2022; 88: 100956, https://doi.org/10.1016/j.pecs.2021.100956

Kaiser RI, Hansen, N
An aromatic universe – a physical chemistry perspective
Journal of Physical Chemistry A, 2021; 125: 3826-3840, https://doi.org/10.1021/acs.jpca.1c00606

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Physical Chemistry Chemical Physics 2020; 22(9): 5314–5331, https://doi.org/10.1039/D0CP00116C

Michelsen HA, et al.
A review of terminology used to describe soot formation and evolution under combustion and pyrolytic conditions
ACS Nano, 2020; 14: 12470-1249, https://dx.doi.org/10.1021/acsnano.0c06226

Wang Y, Chung SH
Soot formation in laminar counterflow flames
Progress in Energy and Combustion Science 2019; 74: 152–238, https://doi.org/10.1016/j.pecs.2019.05.003

Michelsen HA
Probing soot formation, chemical and physical evolution, and oxidation: A review of in situ diagnostic techniques and needs
Proceedings of the Combustion Institute 2017; 36(1): 717–35, https://doi.org/10.1016/j.proci.2016.08.027

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Proceedings of the Combustion Institute 2011; 33(1): 41–67, https://doi.org/10.1016/j.proci.2010.09.009

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Proceedings of the Combustion Institute 2009; 32: 593–613. https://doi.org/10.1016/j.proci.2008.09.005

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Progress in Energy and Combustion Science 2000; 26(4-6): 565–608 https://doi.org/10.1016/S0360-1285(00)00009-5

GAS PHASE CHEMICAL PHYSICS

GAS PHASE CHEMICAL PHYSICS

Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

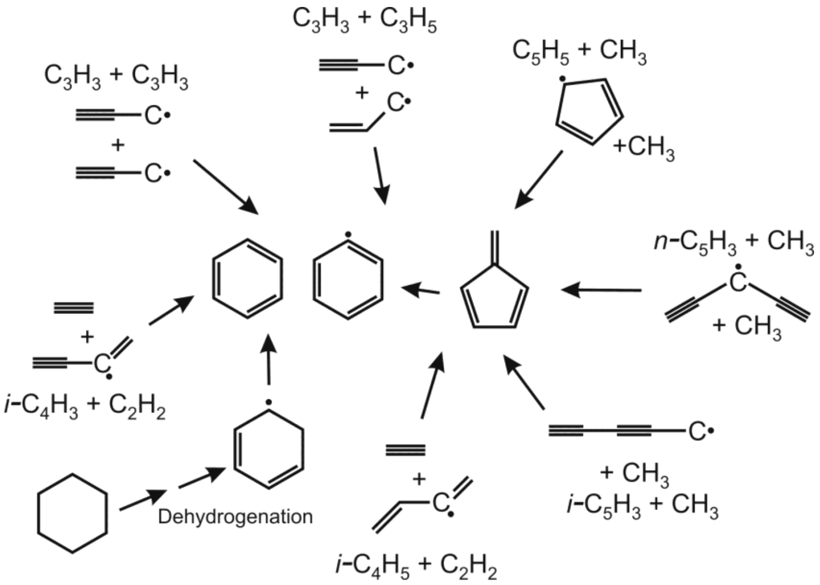
Lecture 2: Formation of the First Aromatic Ring

Nils Hansen

Sandia National Laboratories

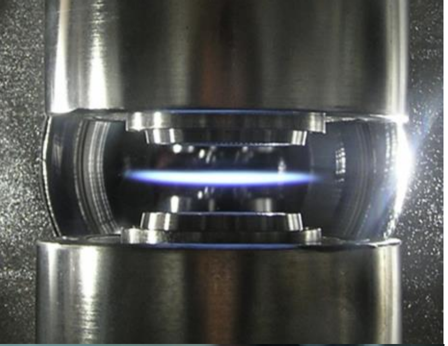
COMBUSTION RESEARCH FACILITY
CRF
SANDIA NATIONAL LABORATORIES / CALIFORNIA

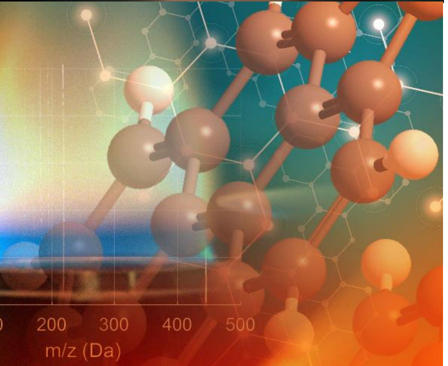
Formation of Benzene



- ✓ many different reactions can contribute towards benzene formation
- ✓ they all involve resonantly stabilized radicals
- ✓ the importance of these reactions depends on the fuel consumption pathways
- ✓ fulvene is an important intermediate

N. Hansen *et al., Prog. Energy Combust. Sci.*, **2009,** 35(2), 168-191
N. Hansen *et al., Combust. Expl. Shock Waves,* **2012,** 48, 508-515





Fuel-Structure Dependence of Benzene Formation

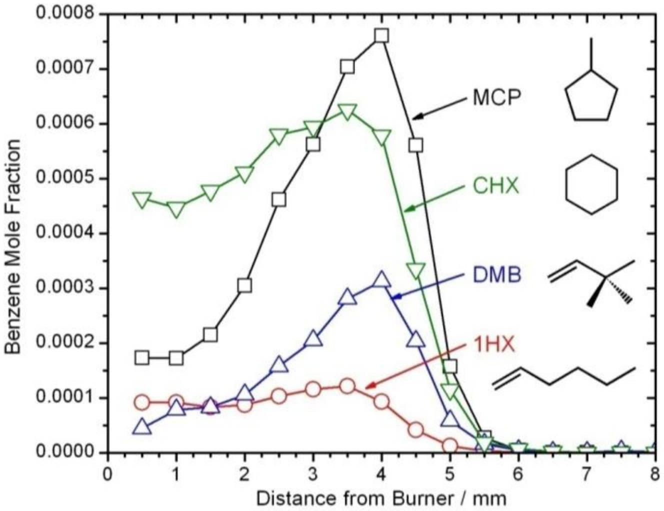
1-Hexene

3,3-Dimethyl-1-Butene

Methyl-cyclopentane

Cyclohexane

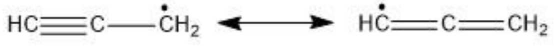
- selected fuels represent a variety of chemical structures, including *alkenes*, a *branched alkene*, an *alkyne*, a *cycloalkene*, a *cycloalkane*, and its *methyl-substituted* derivative



N. Hansen *et al., Proc. Combust. Inst.*, **2011,** 33, 585-592

Propargyl + Propargyl ($C_3H_3 + C_3H_3$)

Resonantly stabilized radical:



- reduces the reactivity (not susceptible to oxidation, i.e., not forming strong bonds with O)
- propargyl is stable enough to accumulate in substantial concentrations

Formed via: $^1CH_2 + C_2H_2 \rightleftarrows C_3H_3 + H$
or H-abstraction or fuel fragmentation

First suggested by Miller and Melius (*Combust. Flame,* **1992,** 91, 21-39)

- ✓ radical-radical reactions can occur at much higher rates than radical-molecule reactions
- ✓ the bond formed in the initial adduct of these reactions is expected to be much stronger than that of the radical-molecule reactions, thus providing greater opportunity for rearrangement and cyclization

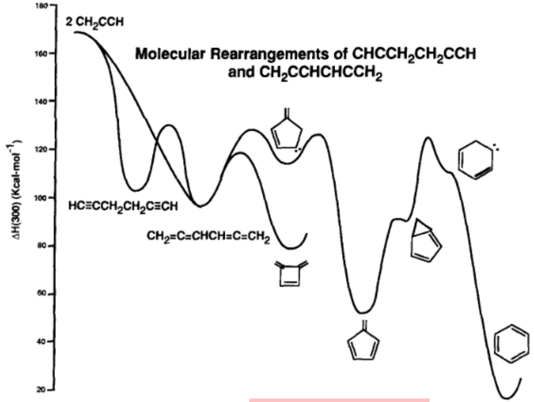


Fig. 10. Reaction coordinate diagram for head-to-head and tail-to-tail recombination of propargyl radicals (the CH_2 end of propargyl is called the head, the CH end the tail).

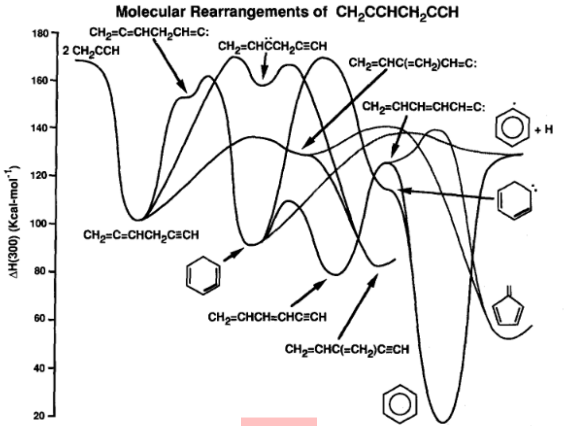
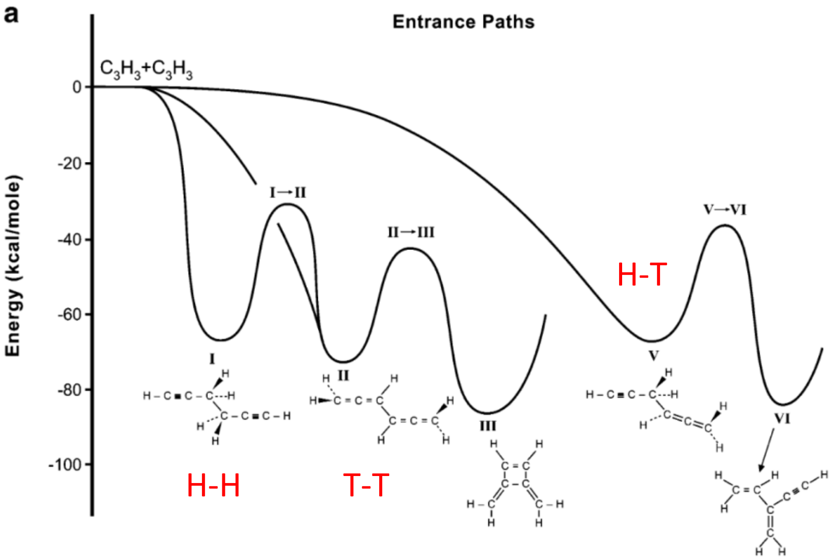
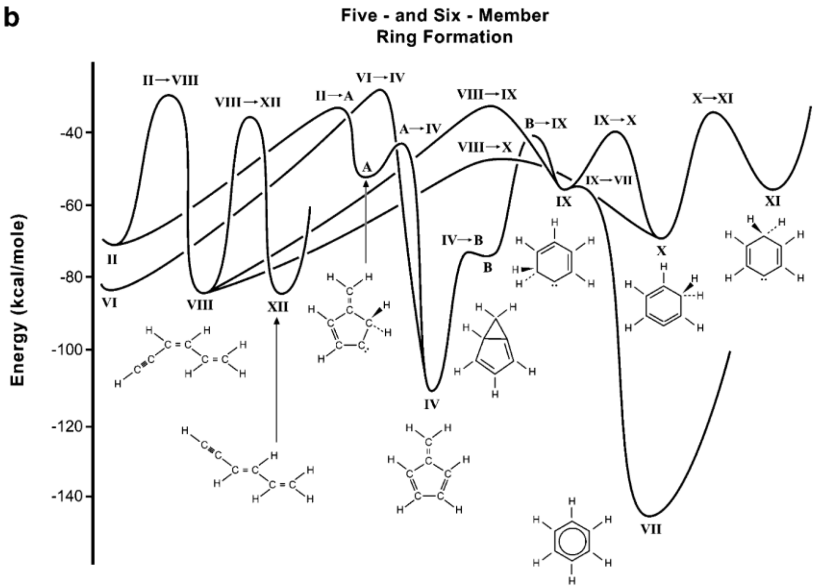


Fig. 11. Reaction coordinate diagram for head-to-tail recombination of propargyl radicals (the CH_2 end of propargyl is called the head, the CH end the tail).

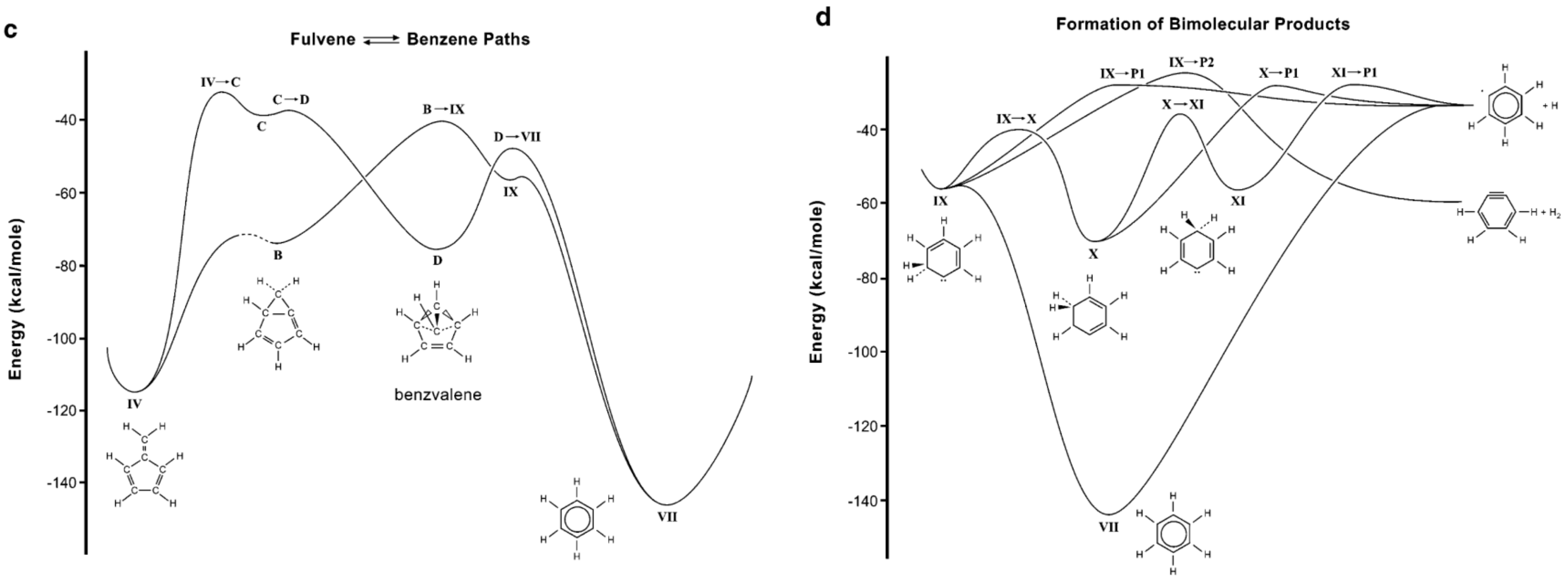
Propargyl + Propargyl ($C_3H_3 + C_3H_3$)





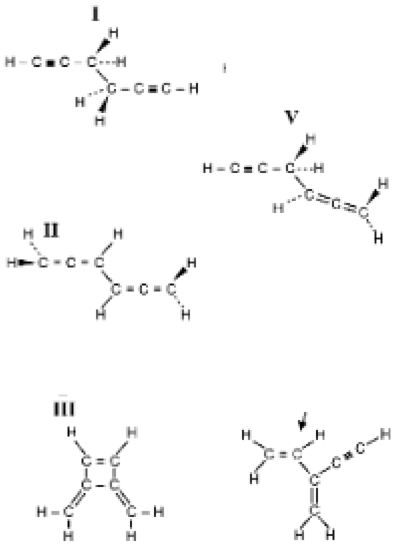
J. A. Miller, S. J. Klippenstein, "The Recombination of Propargyl Radicals and Other Reactions on the C_6H_6 Potential", *J. Phys. Chem. A,* **2003,** 107, 7783-7799

Propargyl + Propargyl ($C_3H_3 + C_3H_3$)



J. A. Miller, S. J. Klippenstein, "The Recombination of Propargyl Radicals and Other Reactions on the C_6H_6 Potential", *J. Phys. Chem. A,* **2003,** 107, 7783-7799

Propargyl + Propargyl (C_3H_3 + C_3H_3)



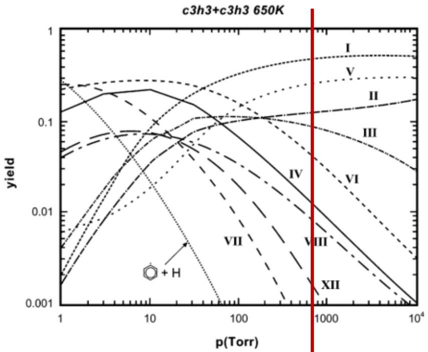


Figure 14. Product distribution for C_3H_3 + C_3H_3 → products as a function of pressure at T = 650 K.

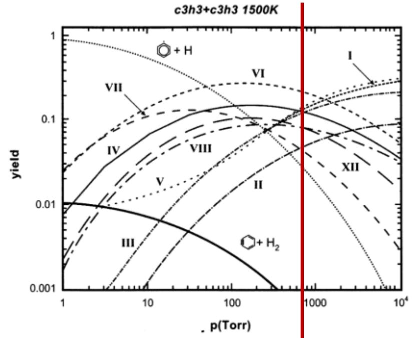
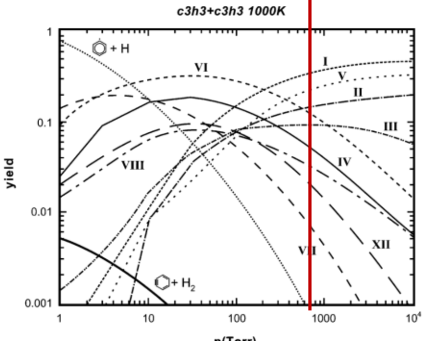
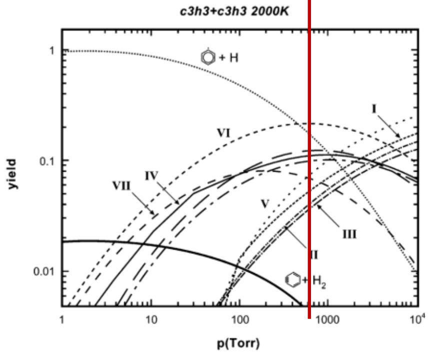


Figure 16. Product distribution for C_3H_3 + C_3H_3 → products as a function of pressure at T = 1500 K.





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Propargyl + Propargyl ($C_3H_3 + C_3H_3$)

Experimental Validation

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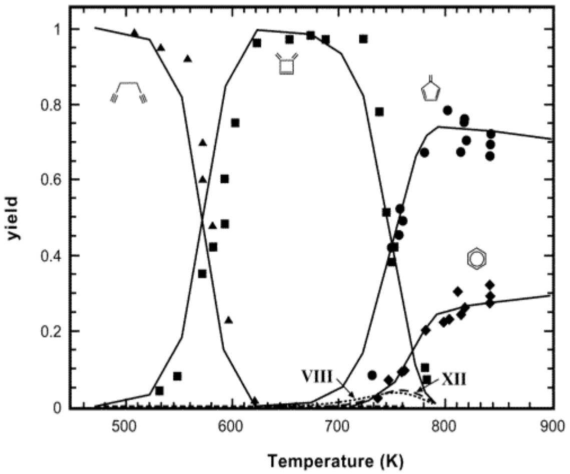
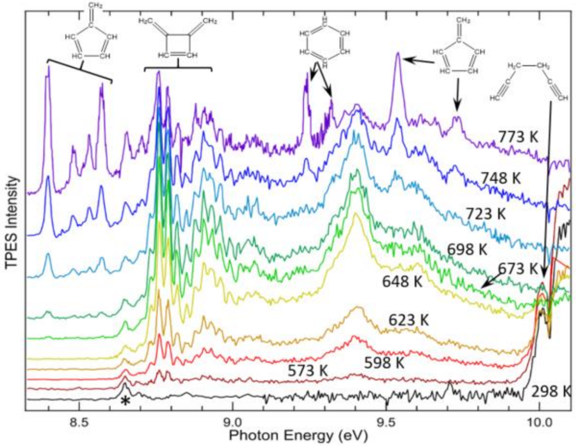
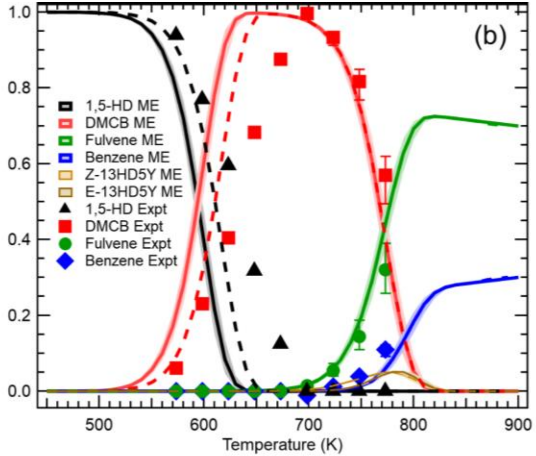
Propargyl + Propargyl ($C_3H_3 + C_3H_3$)

Experimental validation – low temperatures:



J. A. Miller, S. J. Klippenstein, “The Recombination of Propargyl Radicals and Other Reactions on the C_6H_6 Potential”, *J. Phys. Chem. A,* **2003,** 107, 7783-7799

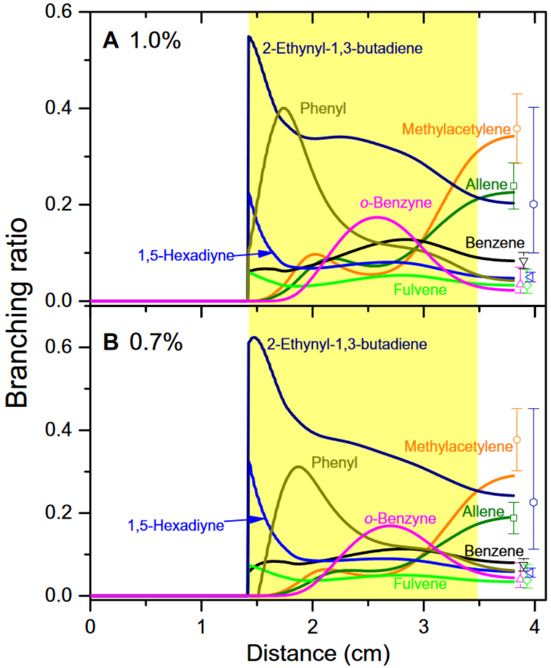


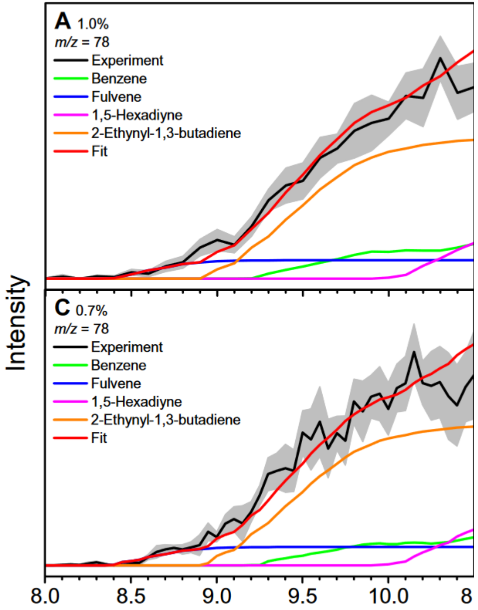


J. D. Savee *et al.,* “Unimolecular Isomerisation of 1,5-Hexadiyne observed by Threshold Photoelectron Photoion Coincidence Spectroscopy”, *Faraday Disc.,* **2023**

Propargyl + Propargyl (C_3H_3 + C_3H_3)

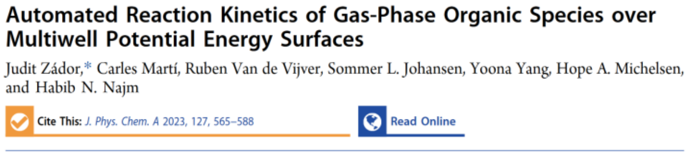
Experimental validation – high temperatures:





L. Zhao *et al.,* "Gas-phase synthesis of benzene via the propargyl radical self reaction", *Sci. Adv.,* **2021,** 7(21), eabf0360, DOI: 10.1126/sciadv.abf0360

Propargyl + Propargyl ($C_3H_3 + C_3H_3$)



Automated Reaction Kinetics of Gas-Phase Organic Species over Multiwell Potential Energy Surfaces

Judit Zádor,* Carles Martí, Ruben Van de Vijver, Sommer L. Johansen, Yoona Yang, Hope A. Michelsen, and Habib N. Najm

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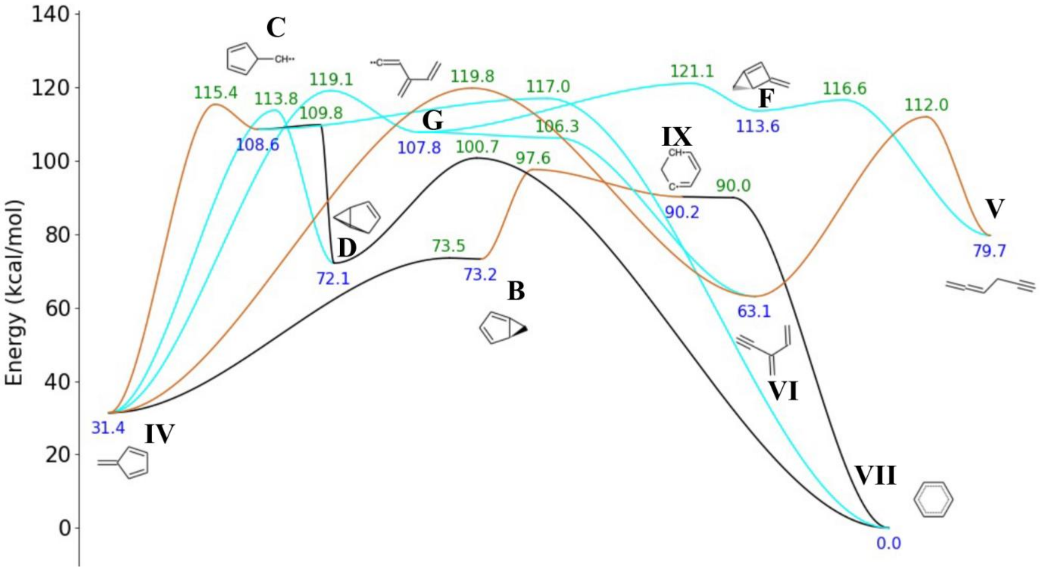

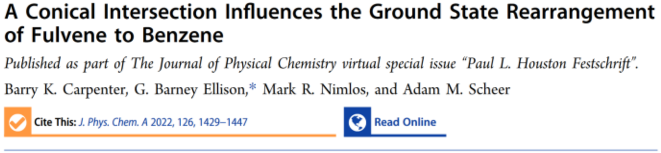

A Conical Intersection Influences the Ground State Rearrangement of Fulvene to Benzene

Published as part of The Journal of Physical Chemistry virtual special issue "Paul L. Houston Festschrift".

Barry K. Carpenter, G. Barney Ellison,* Mark R. Nimlos, and Adam M. Scheer

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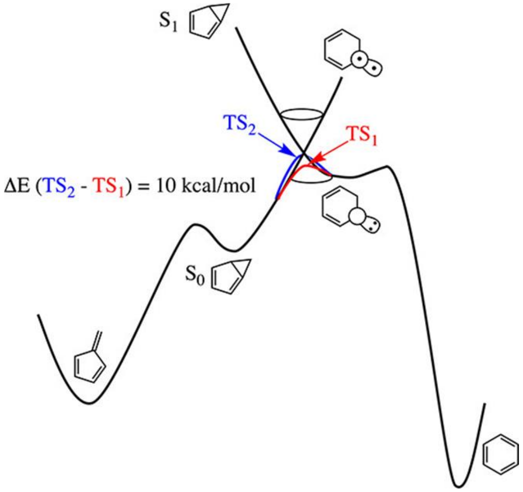
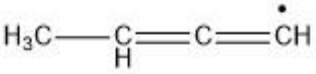


i-/*n*-C_4H_5 + C_2H_2

Methyl-substituted C_3H_3

$H_3C{-}C{\equiv}C{-}\dot{C}H_2$

Methyl-substituted C_3H_3

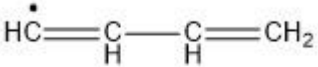


$H_3C{-}CH{=}C{=}\dot{C}H$

i-C_4H_5 – resonantly stabilized radical

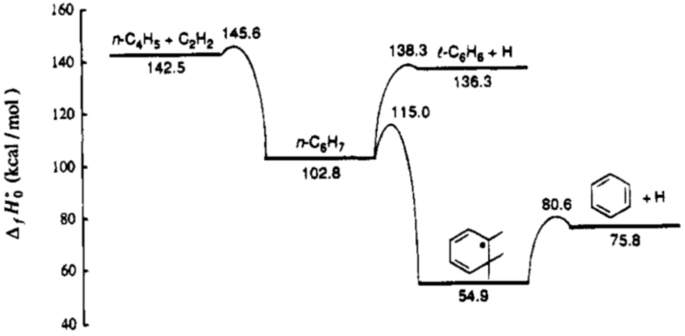
$H_2C{=}CH{-}\dot{C}{=}CH_2$

n-C_4H_5 – non-resonantly stabilized radical

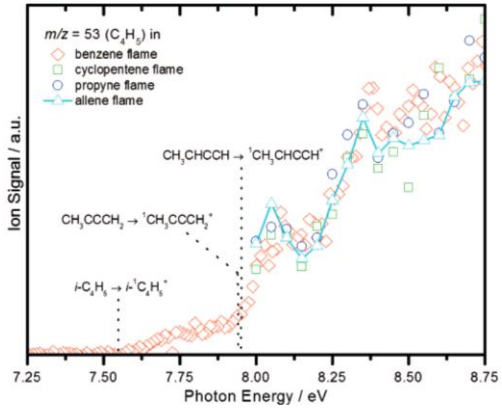


$H\dot{C}{=}CH{-}CH{=}CH_2$

Miller and Melius (Combust. Flame, **1992,** 91, 21-39) suggested this radical-molecule reaction to be competitive to radical-radical reactions

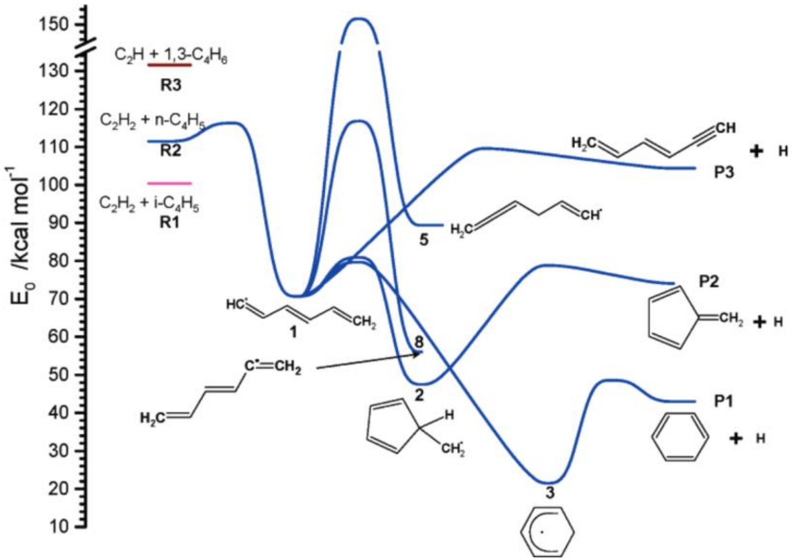


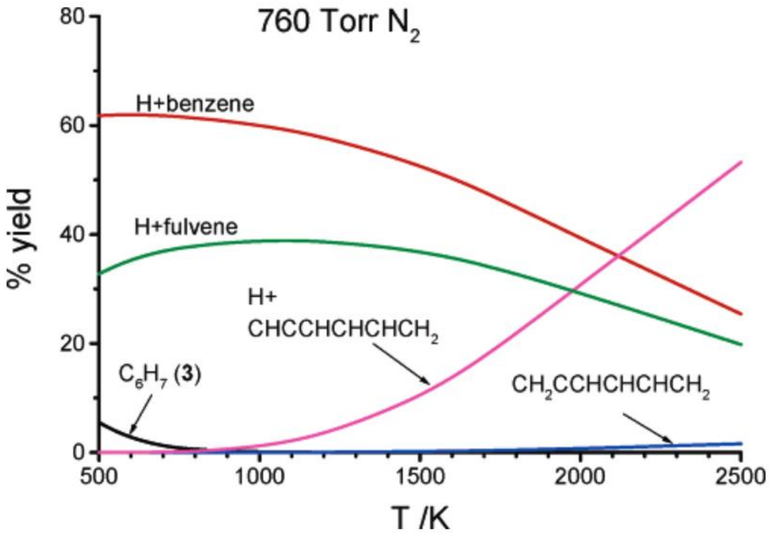
Wang and Frenklach, *J. Phys. Chem.*, **1994,** 98, 11465-11489



N. Hansen *et al.*, *"*Identification and Chemistry of C_4H_3 and C_4H_5 Isomers in Fuel-Rich Flames," *J. Phys. Chem. A,* **2006,** 110, 3670-3678

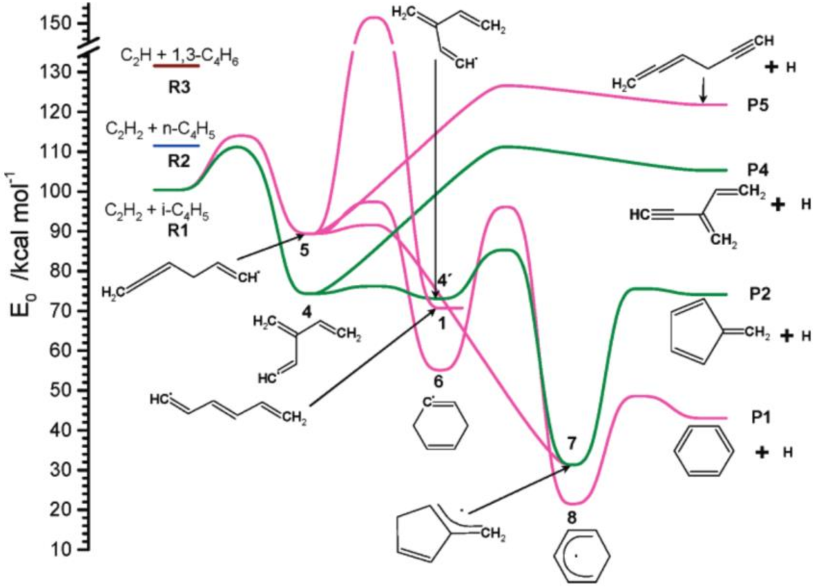
i-/n-C_4H_5 + C_2H_2

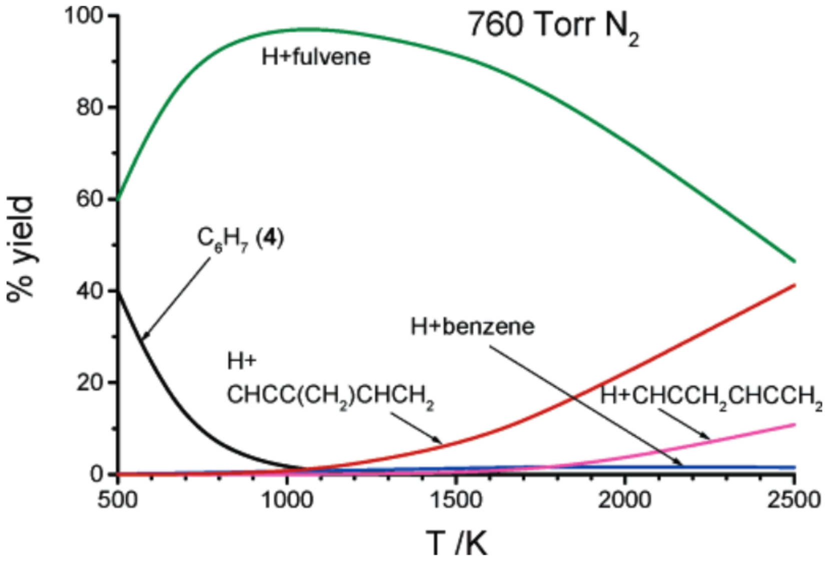




J. P. Senosiain and J. A. Miller, "The Reaction of *n*- and *i*-C_4H_5 Radicals with Acetylene", *J. Phys. Chem. A,* **2007,** 111, 3740-3747

i-/*n*-$C_4H_5 + C_2H_2$

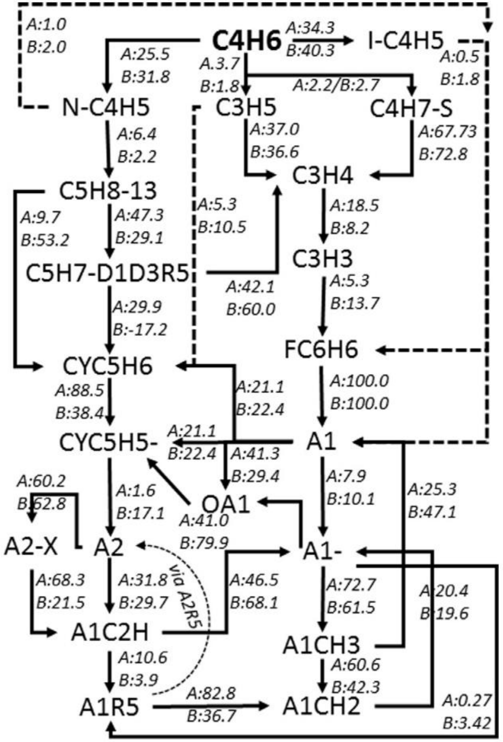




J. P. Senosiain and J. A. Miller, "The Reaction of *n*- and *i*-C_4H_5 Radicals with Acetylene", *J. Phys. Chem. A,* **2007,** 111, 3740-3747

i-/*n*-C_4H_5 + C_2H_2

i-C_4H_5 + H $\rightleftarrows$ C_3H_3 + CH_3 is fast, thus limiting the importance of *i*-C_4H_5

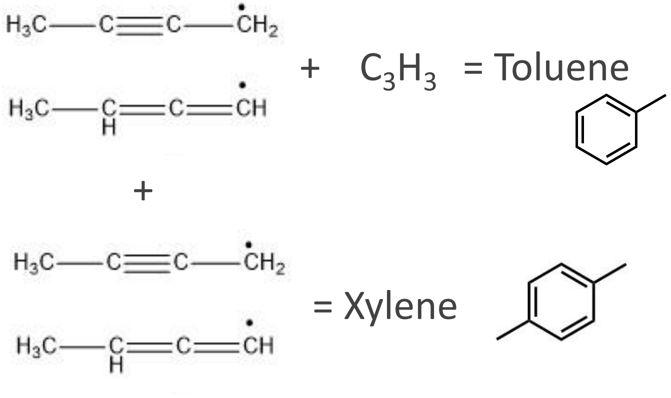


Mostly found important in 1,3-butadien flames:

- N. Hansen et al., “Benzene Formation in Premixed Fuel-Rich 1,3-Butadiene Flames”, Proc. Combust. Inst., 2009, 32, 623-630

  first to show that C3H3+C3H3 and i-C4H5+C2H2 contribute equally
- N. Hansen et al., “Fuel-Structure Dependence of Benzene Formation Processes in Premixed Flames Fueled by C6H12 Isomers, 2011, 33, 585-592
- K. Moshammer et al., “Aromatic Ring Formation in Opposed-Flow Diffusive 1,3-Butadiene Flames, Proc. Combust. Inst., 2017, 36, 947-955

Possible reactions of methyl-substituted propargyl radicals:



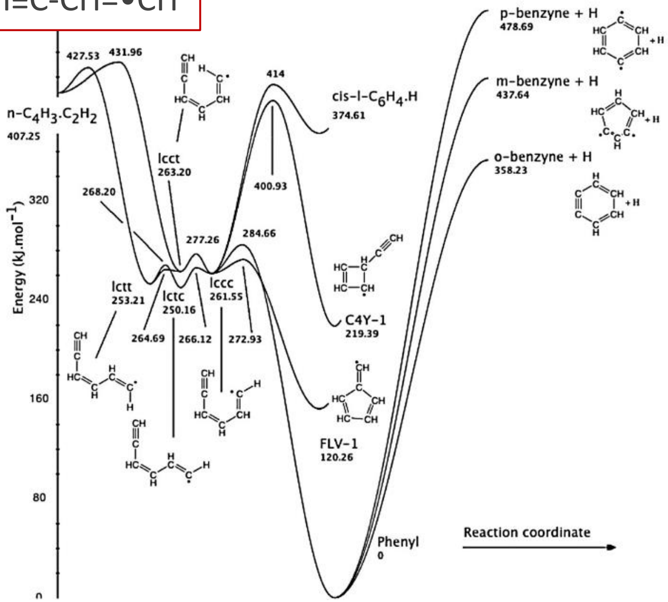
GAS PHASE CHEMICAL PHYSICS

i-/n-C_4H_3 + C_2H_2

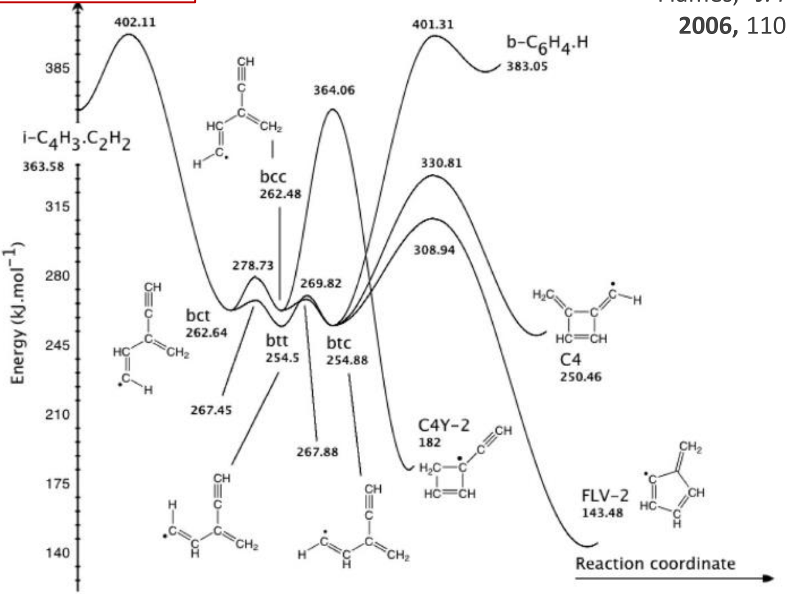
to my knowledge not convincingly shown to be important
C_4H_3 is not accumulating in large enough concentrations

***i*-C_4H_3 identified in flames**
N. Hansen *et al.*,
"Identification and Chemistry of C_4H_3 and C_4H_5 Isomers in Fuel-Rich Flames," *J. Phys. Chem. A,* **2006,** 110, 3670-3678

CH≡C-CH=•CH



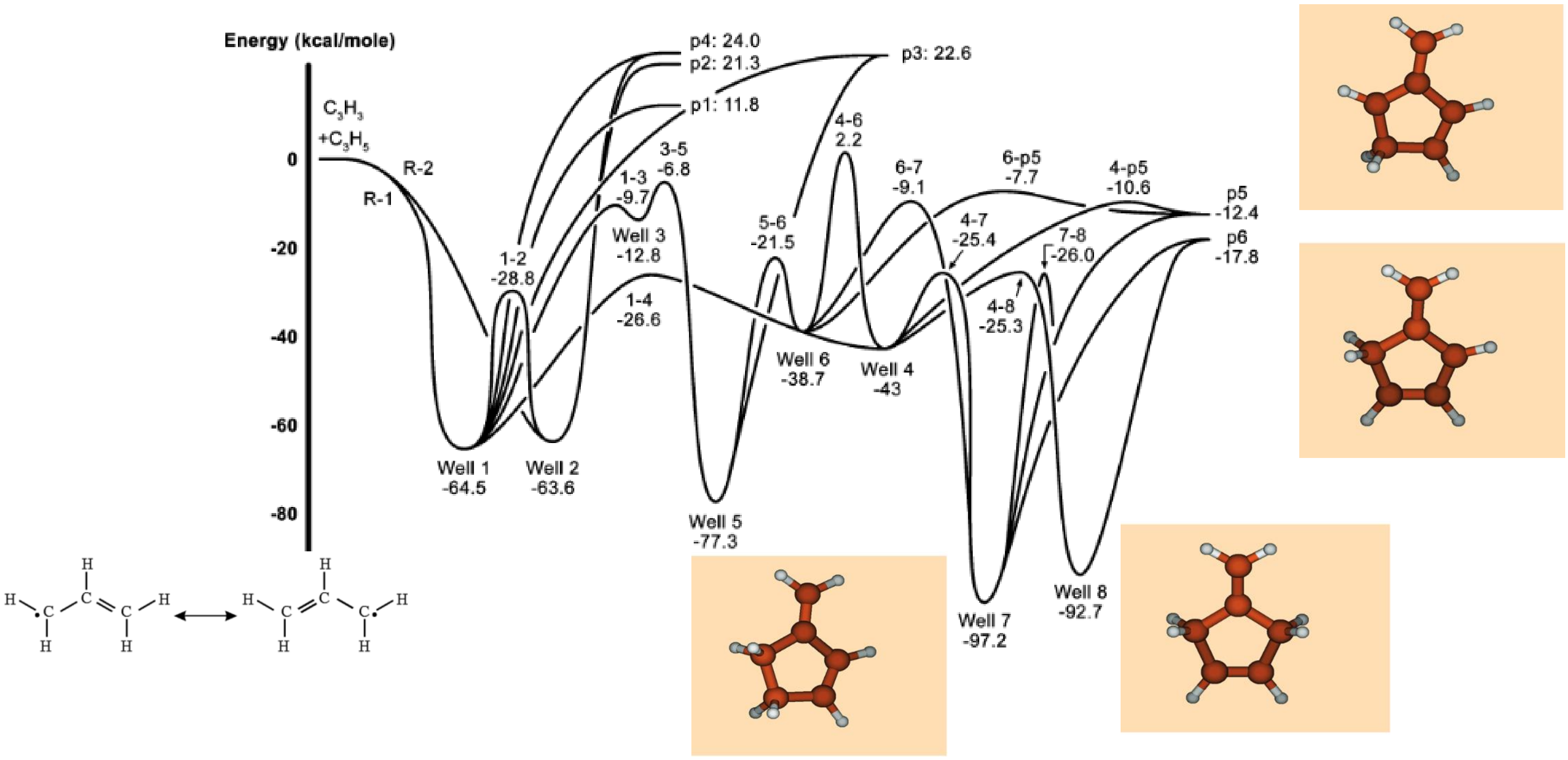
CH≡C-C•=CH_2



X. Lories, J. Vandooren, D. Peeters, "Cycle Formation from Acetylene Addition on C_4H_3 Radicals", *Phys. Chem. Chem. Phys.,* **2010,** 12, 3762-3771

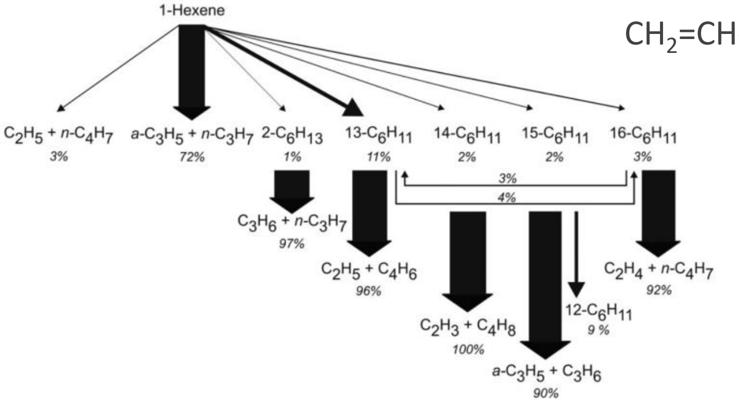
Also look at: E. Wang, J. Ding, K. Han, "Reaction between i-C4H3 Radical and Acetylene (C2H2): Is Phenyl (C6H5) the Primary Product?", *Energy Fuels,* **2018,** 32, 5581-5587

$C_3H_5 + C_3H_3 \rightleftarrows$ Fulvene + H + H

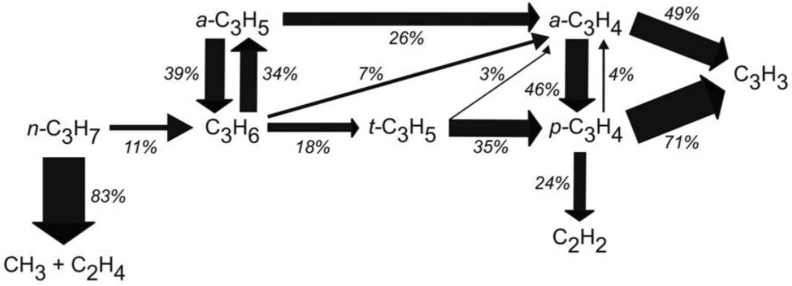


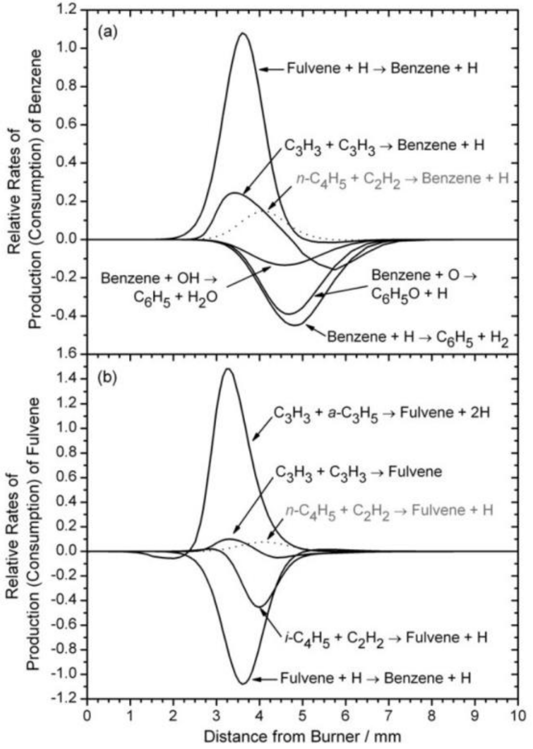
Miller et al., “Reactions between Resonance-Stabilized Radicals: Propargyl + Allyl“, *J. Phys. Chem. A,* **2010,** 114-4881-4890

$C_3H_5 + C_3H_3 \rightleftarrows$ Fulvene + H + H



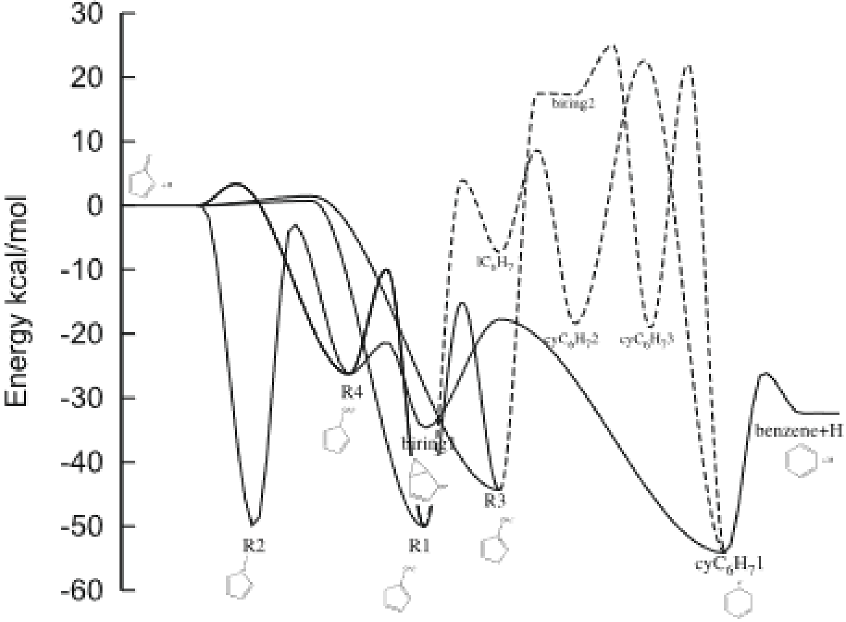
CH_2=CH-CH_2-CH_2-CH_2-CH_3



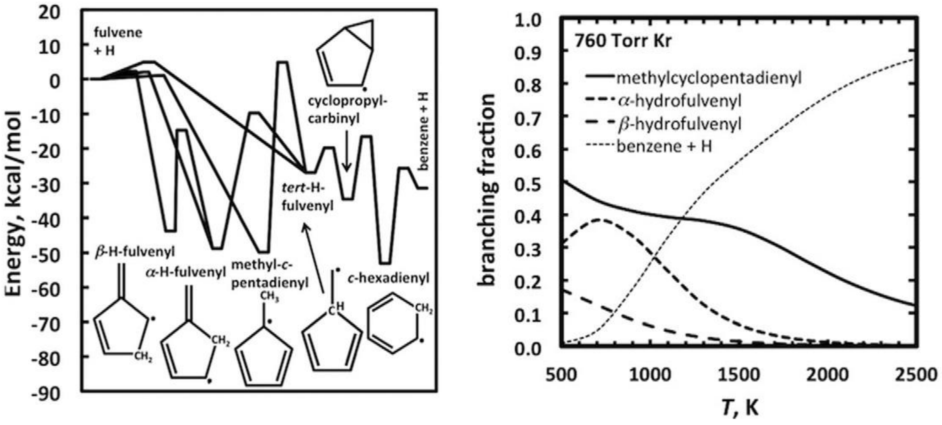


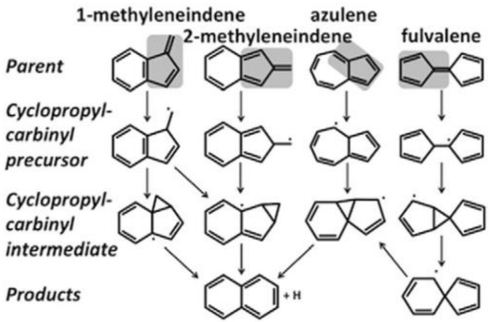
N. Hansen *et al.,* "The Importance of Fuel Dissociation and Propargyl + Allyl Association for the Formation of Benzene in a Fuel-Rich 1-Hexene Flame", Phys. Chem. Chem. Phys., **2010,** 12, 12112-12122

Fulvene + H = Benzene + H



S. Sharma, M. R. Harper, W. H. Green, “Modeling of 1,3-hexadiene, 2,4-hexadiene, and 1,4-hexadiene-doped methane flames: Flame modeling, benzene and styrene formation”, *Combust. Flame,* **2010,** 157, 1331-1345

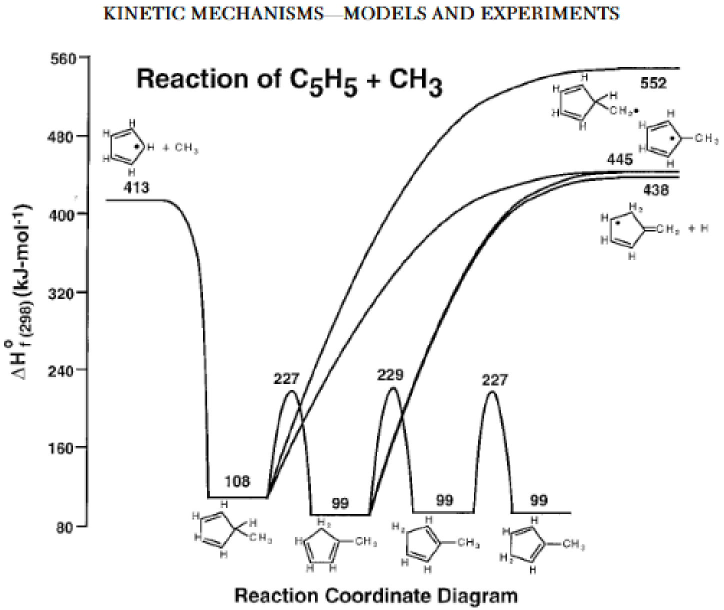




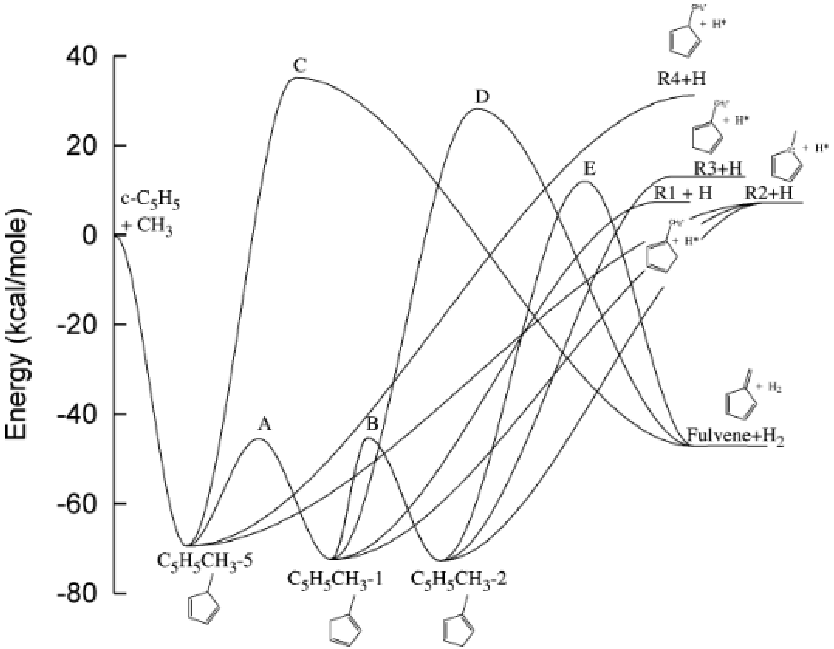
A. W. Jasper, N. Hansen, “Hydrogen-assisted isomerizations of fulvene to benzene and of larger cyclic aromatic hydrocarbons”, *Proc. Combust. Inst.,* **2013,** 34, 279-287

$C_5H_5 + CH_3$ = Fulvene/Benzene + H + H

C. F. Melius *et al.*, "Reaction mechanisms in aromatic hydrocarbon formation involving the C_5H_5 cyclopentadienyl", *Proc. Combust. Inst.*, **1996,** 26, 685-692

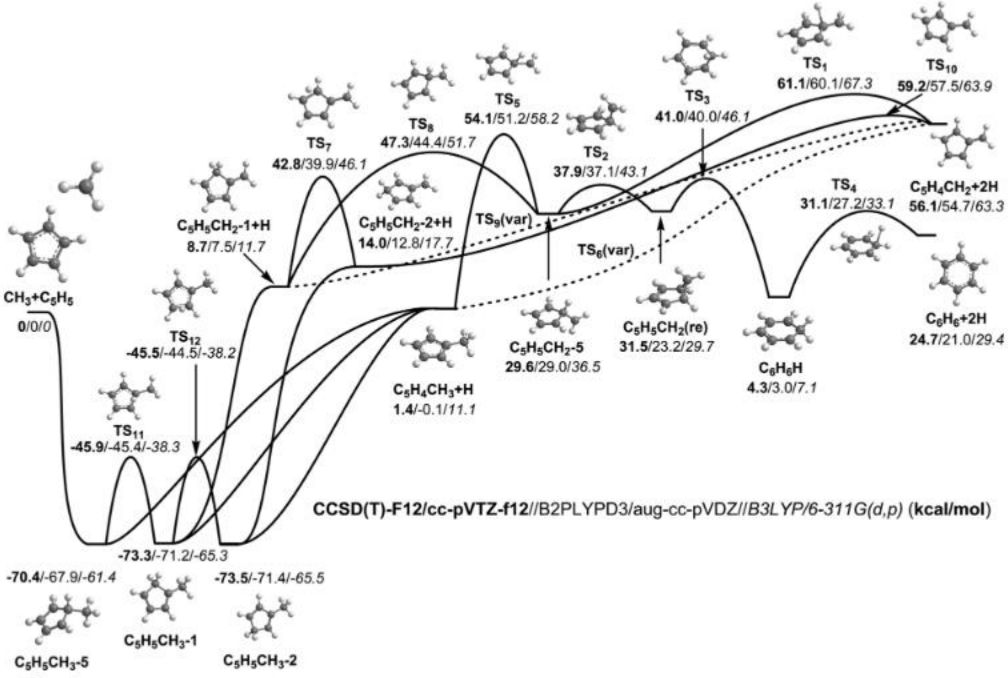


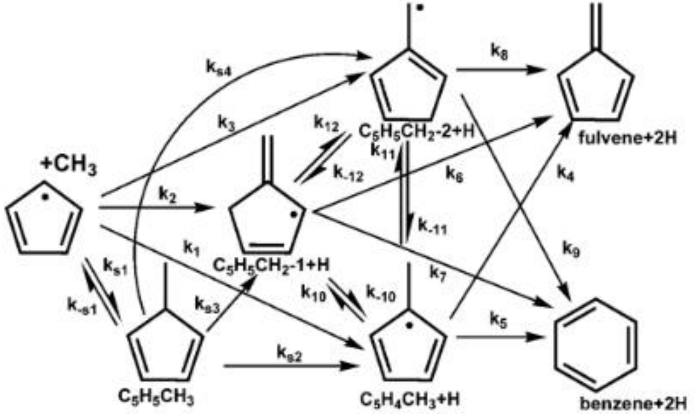
S. Sharma, W. H. Green, "Computed Rate Coefficients and Product Yields for c-$C_5H_5 + CH_3$ = Products", *J. Phys. Chem. A*, **2009,** 113, 8871-8882



L. V. Moskaleva *et al.*, "The $CH_3 + C_5H_5$ Reaction: A Potential Source of Benzene at High Temperatures", *Proc. Combust. Inst.*, **1996,** 26, 521-526

$C_5H_5 + CH_3$ = Fulvene/Benzene + H + H



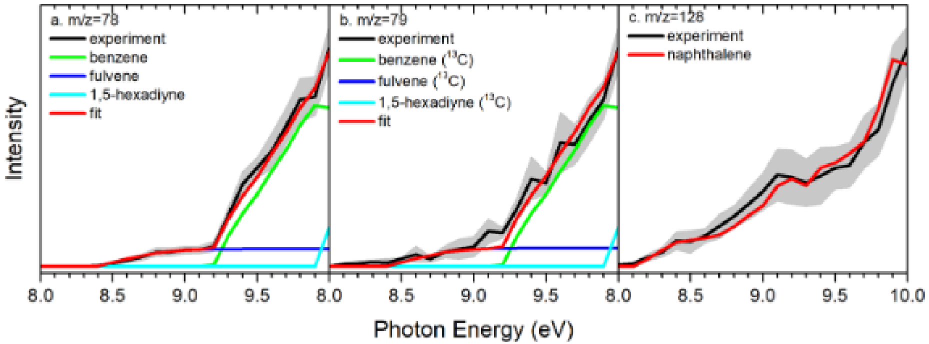


V. S. Krasnoukhov *et al.*, "Kinetics of the $CH_3 + C_5H_5$ Reaction: A Theoretical Study", *J. Phys. Chem. A,* **2017,** 121, 48, 9191–9200

GAS PHASE CHEMICAL PHYSICS

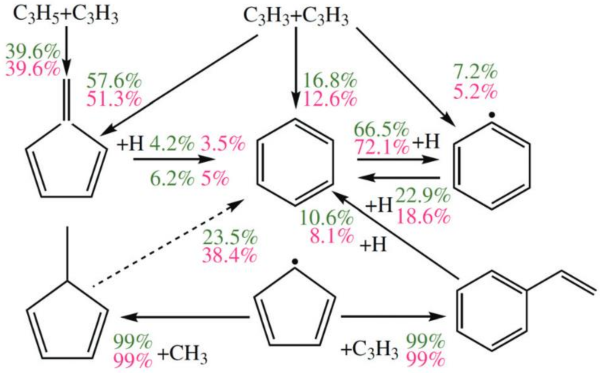
$C_5H_5 + CH_3$ = Fulvene/Benzene + H + H

Reactor Experiments:



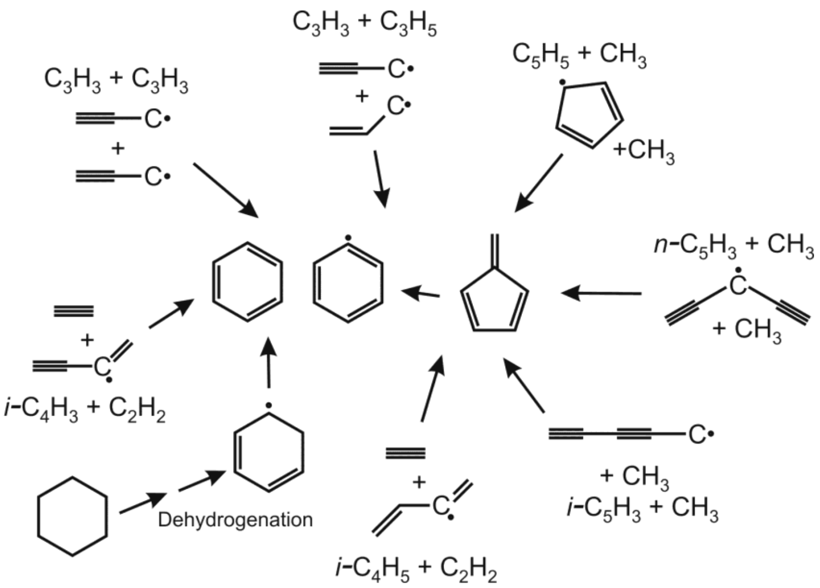
R. I. Kaiser *et al.,* “Formation of Benzene and Naphthalene through Cyclopentadienyl-Mediated Radical-Radical Reactions”, *J. Phys. Chem. Lett.,* **2022,** 13, 208-213

Flame Experiments:



M. Baroncelli *et al.,* “Role of ring-enlargement reactions in the formation of aromatic hydrocarbons”, *Phys. Chem. Chem. Phys.,* **2020,** 22, 4699-4714

Conclusion: Formation of Benzene is complicated



- ✓ many different reactions can contribute towards benzene formation
- ✓ they all involve resonantly stabilized radicals
- ✓ the importance of these reactions depends on the fuel consumption pathways
- ✓ fulvene is an important intermediate

N. Hansen *et al., Prog. Energy Combust. Sci.,* **2009,** 35(2), 168-191
N. Hansen *et al., Combust. Expl. Shock Waves,* **2012,** 48, 508-515

GAS PHASE CHEMICAL PHYSICS

Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

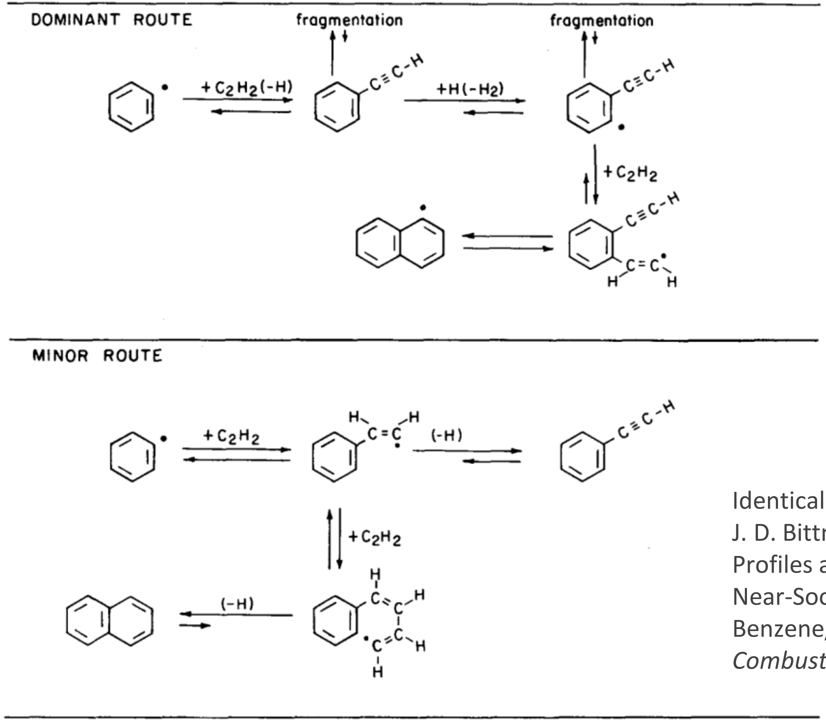
Lecture 3: The HACA Mechanism

Nils Hansen

Sandia National Laboratories

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

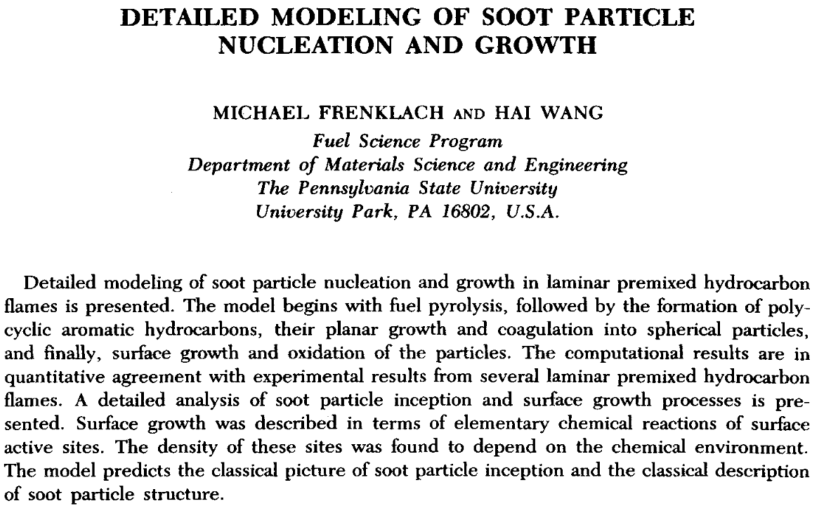


Identical to:
J. D. Bittner, J. B. Howard, “Composition Profiles and Reaction Mechanisms in a Near-Sooting Premixed Benzene/Oxygen/Argon Flame”, *Proc. Combust. Inst.,* **1981,** 18, 1105-1116

M. Frenklach *et al.*, “Detailed Kinetic Modeling of Soot Formation in Shock-Tube Pyrolysis of Acetylene”, *Proc. Combust. Inst.,* **1984,** 20, 887-901

The HACA Mechanism

H-Abstraction-C_2H_2-Addition



DETAILED MODELING OF SOOT PARTICLE NUCLEATION AND GROWTH

MICHAEL FRENKLACH AND HAI WANG
Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802, U.S.A.

Detailed modeling of soot particle nucleation and growth in laminar premixed hydrocarbon flames is presented. The model begins with fuel pyrolysis, followed by the formation of polycyclic aromatic hydrocarbons, their planar growth and coagulation into spherical particles, and finally, surface growth and oxidation of the particles. The computational results are in quantitative agreement with experimental results from several laminar premixed hydrocarbon flames. A detailed analysis of soot particle inception and surface growth processes is presented. Surface growth was described in terms of elementary chemical reactions of surface active sites. The density of these sites was found to depend on the chemical environment. The model predicts the classical picture of soot particle inception and the classical description of soot particle structure.

- This paper introduced the term HACA (because of the word limit of Symposium papers).

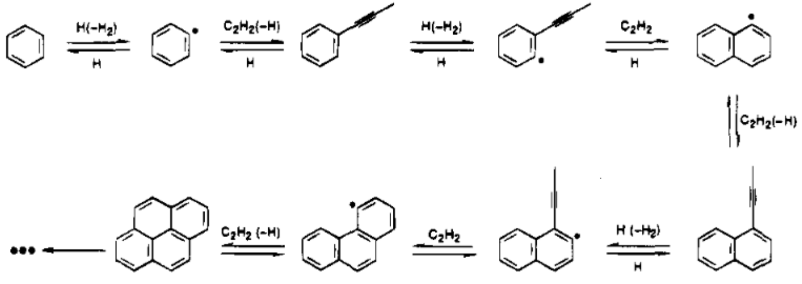
- The detailed mechanism described in that paper includes
  - ✓ fuel pyrolysis
  - ✓ formation of the first aromatic ring *(but not like we talked about it in the previous lecture)*
  - ✓ formation of polycyclic aromatic hydrocarbons
  - ✓ their planar growth and coagulation in spherical particles, and
  - ✓ surface growth and oxidation of the particles.

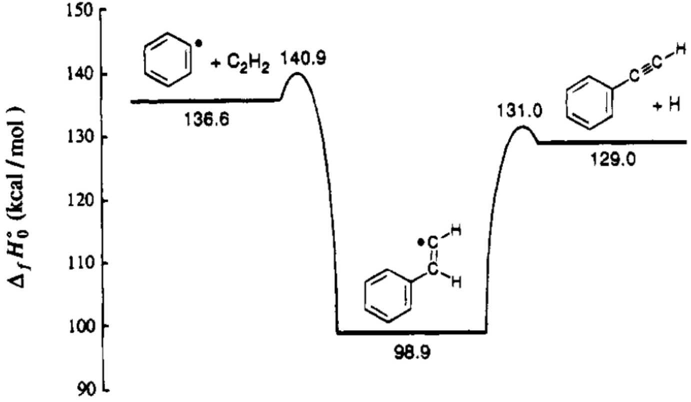
M. Frenklach and H. Wang, “Detailed Modeling of Soot Particle Nucleation and Growth”,
Proc. Combust. Inst., **1990,** 23, 1559-1566

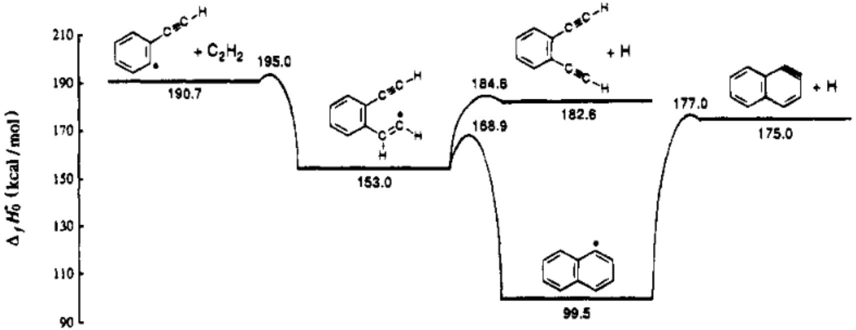
GAS PHASE CHEMICAL PHYSICS

The HACA Mechanism

H-Abstraction-C_2H_2-Addition







- ➢ also includes kinetics of larger PAH – will get to them later
- ➢ implemented in the ABF mechanism:

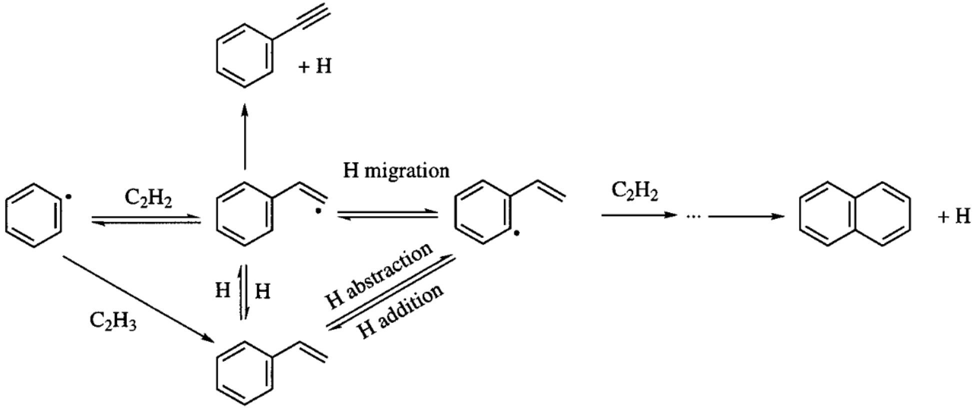
J. Appel, H. Bockhorn, M. Frenklach, “Kinetic Modeling of Soot Formation with Detailed Chemistry and Physics: Laminar Premixed Flames of C2 Hydrocarbons”, *Combust. Flame,* **2000,** 1-2, 122-136

H. Wang and M. Frenklach, “Calculations of Rate Coefficients for the Chemically Activated Reactions of Acetylene with Vinylic and Aromatic Radicals”, *J. Phys. Chem.,* **1994,** 98(44), 11465-11489

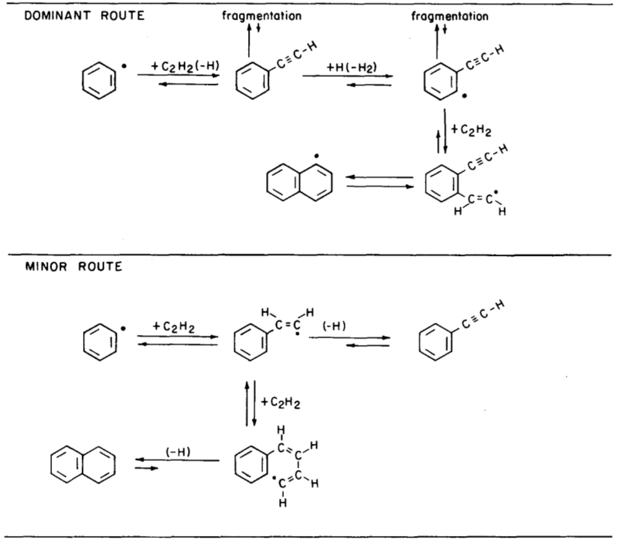
The HACA Mechanism

H-Abstraction-C_2H_2-Addition

Modified:



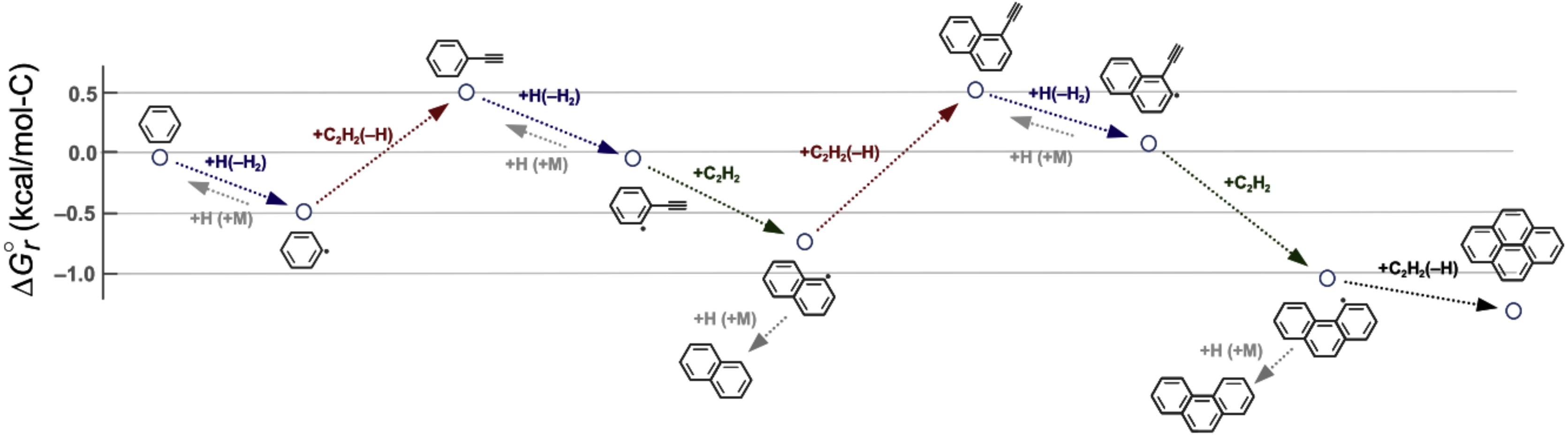
Original:



N. W. Moriarty, N. J. Brown, M. Frenklach, “Hydrogen Migration in the Phenylethen-2-yl-Radical”, *J. Phys. Chem.*, **1999,** 103, 7127-7135

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

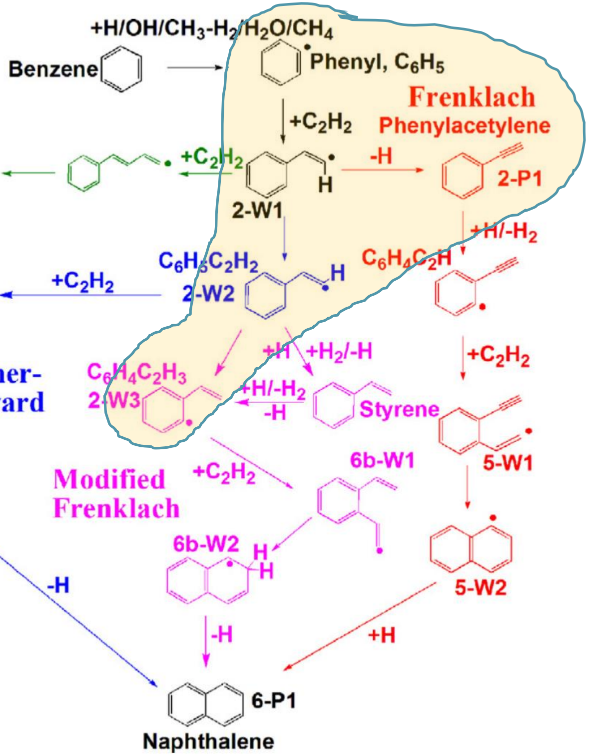


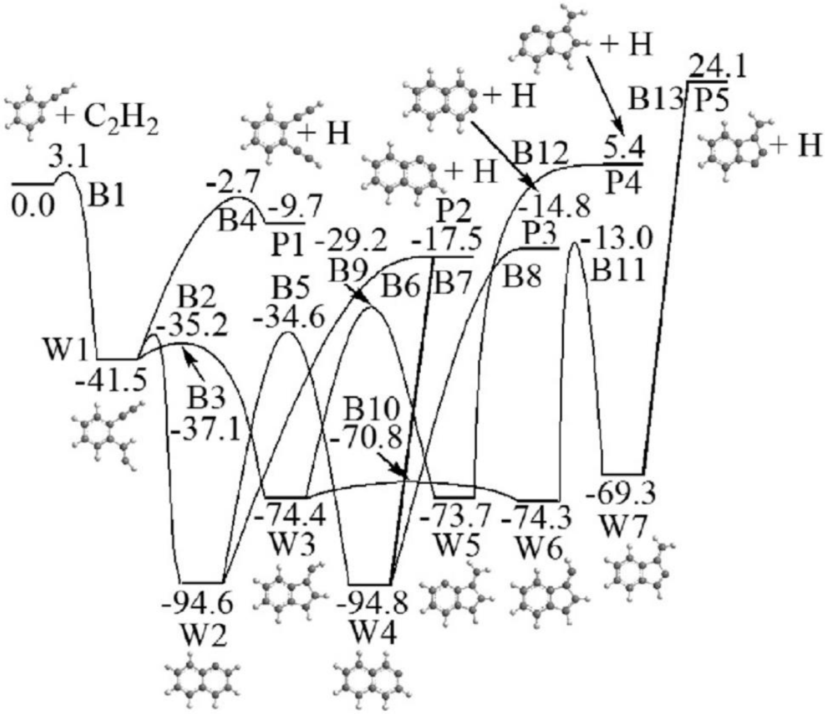
C_2H_2	5	5	4	4	3	2	2	1	0
H	1	0	1	0	0	1	0	0	1
H_2	0	1	1	2	2	2	3	3	3

H. Wang, "Formation of nascent soot and other condensed/phase materials in flames", *Proc. Combust. Inst.*, **2011,** 33, 41-67

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

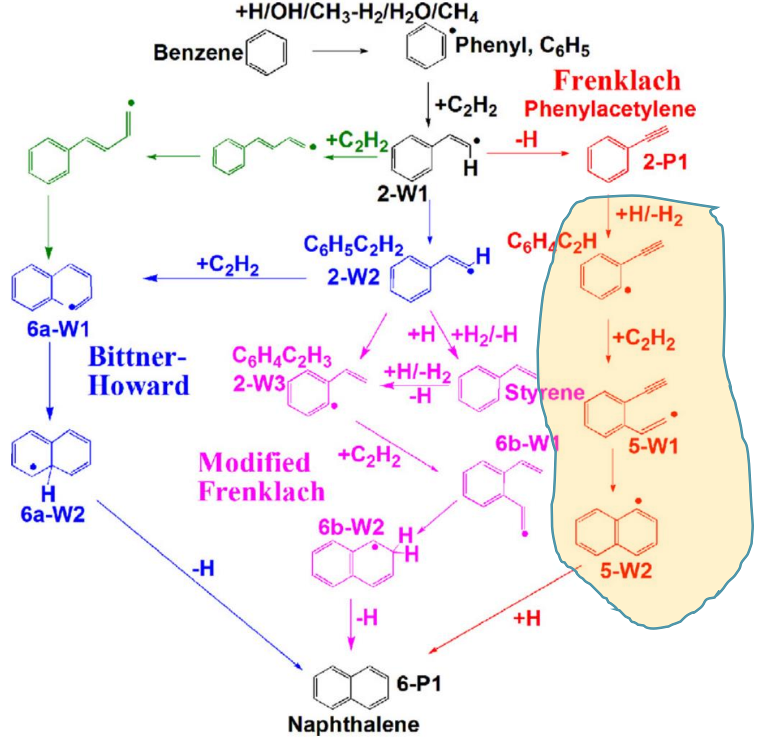


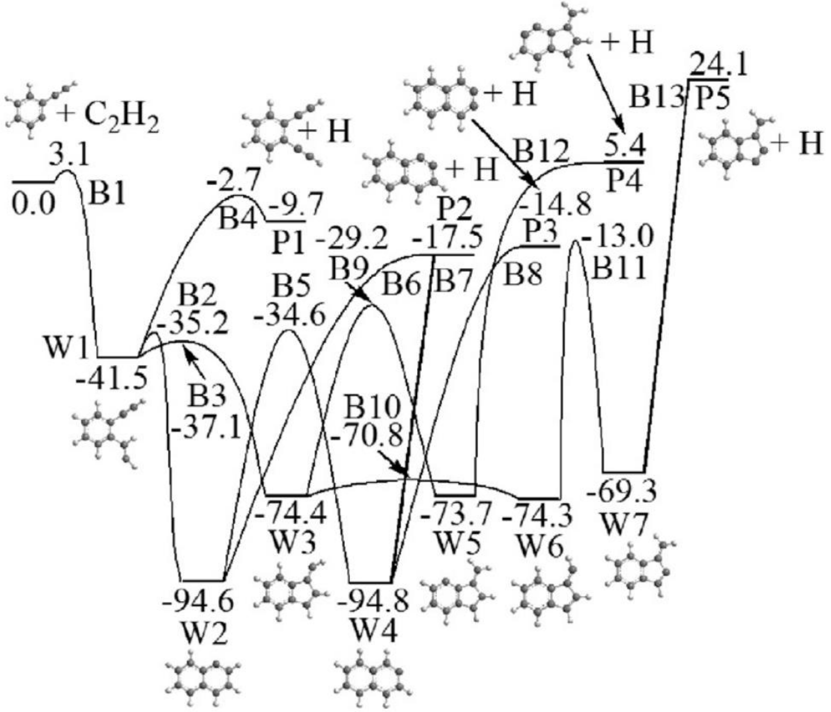


A. M. Mebel, Y. Georgievskii, A. W. Jasper, S. J. Klippenstein, “Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene”, *Proc. Combust. Inst.*, **2017,** 36, 919-926

The HACA Mechanism

H-Abstraction-C_2H_2-Addition



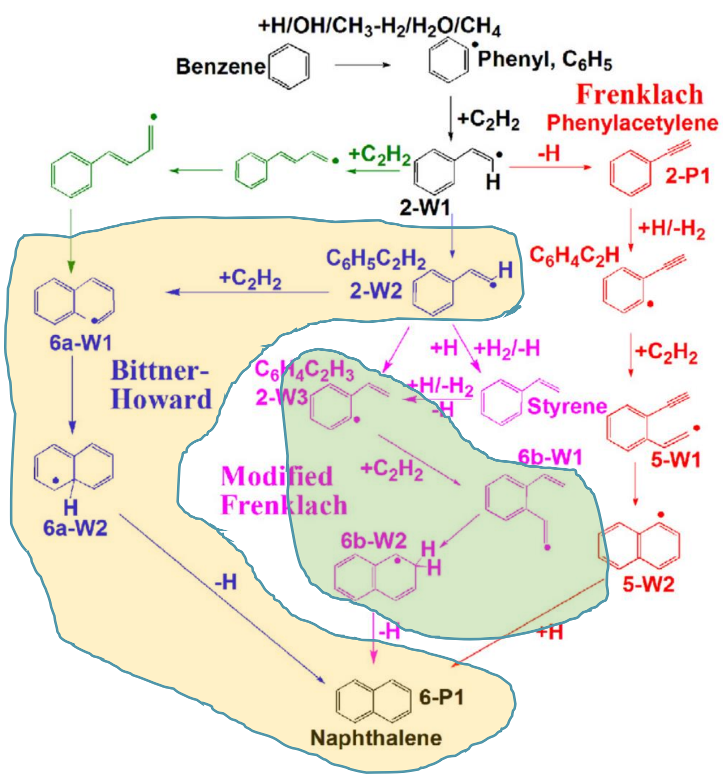


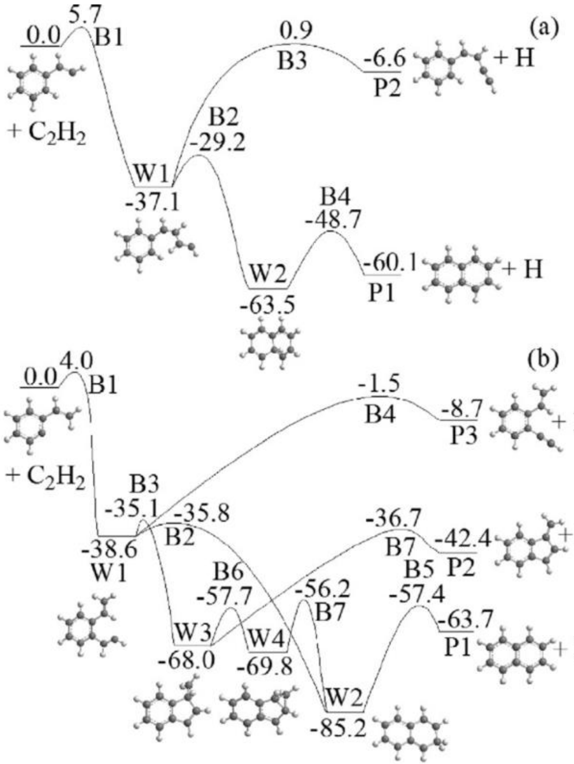
A. M. Mebel, Y. Georgievskii, A. W. Jasper, S. J. Klippenstein, “Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene”, *Proc. Combust. Inst.*, **2017**, 36, 919-926

GAS PHASE CHEMICAL PHYSICS

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

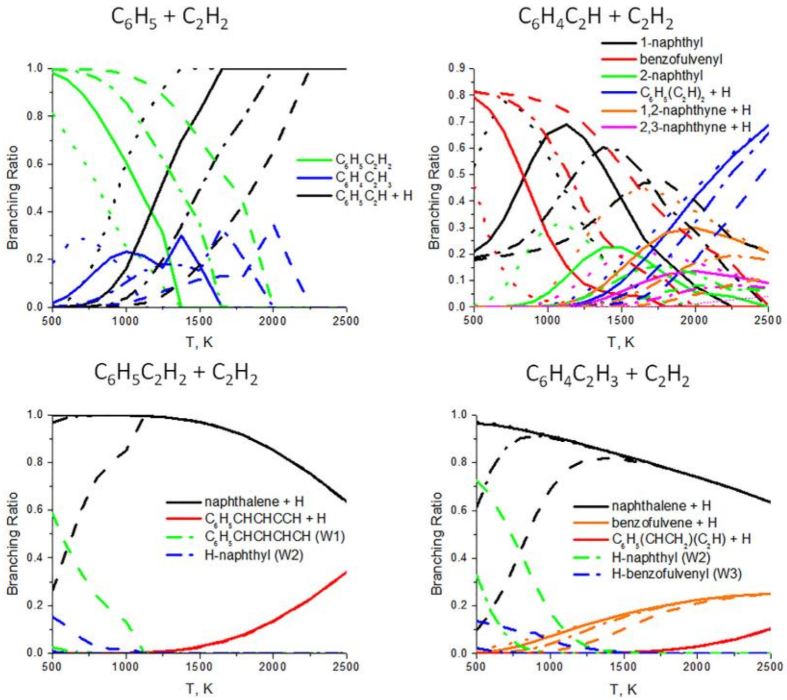




A. M. Mebel, Y. Georgievskii, A. W. Jasper, S. J. Klippenstein, “Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene”, *Proc. Combust. Inst.*, **2017,** 36, 919-926

The HACA Mechanism

H-Abstraction-C_2H_2-Addition



dotted: 30 Torr; **solid:** 1 atm; **dash-dot:** 10 atm; **dash:** 100 atm

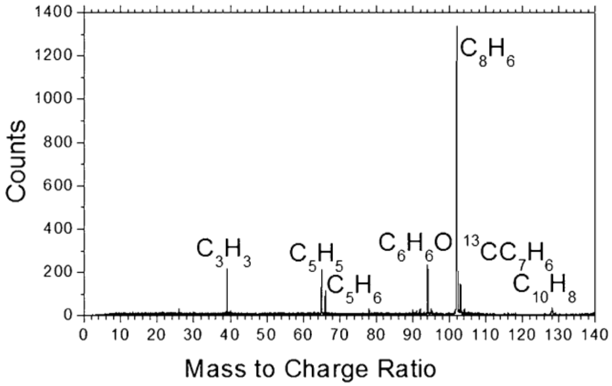
- importance of pressure dependence of the kinetics of naphthalene formation
- the branching amongst various products is strongly dependent on pressure
- C_8H_7 radicals ($C_6H_4C_2H_3$ and $C_6H_5C_2H_2$) are unstable at atmospheric pressure and lower and for temperatures of 1650 K and higher
  - ✓ this makes the Bittner-Howard and the modified Frenklach routes unrealistic under typical low-pressure flame conditions
- at higher pressures, C_8H_7 contribute to the formation of naphthalene (main product of the $C_8H_7 + C_2H_2$ reactions in the 500-2500 K range)
  - ✓ however, the high-temperature reversal of $C_8H_7 = C_6H_5 + C_2H_2$ will greatly hinder that route
- original HACA forms predominantly dehydrogenated naphthalene core (naphthyl radicals or naphthynes) for T below 2000 K and diethynylbenzene at higher temperatures

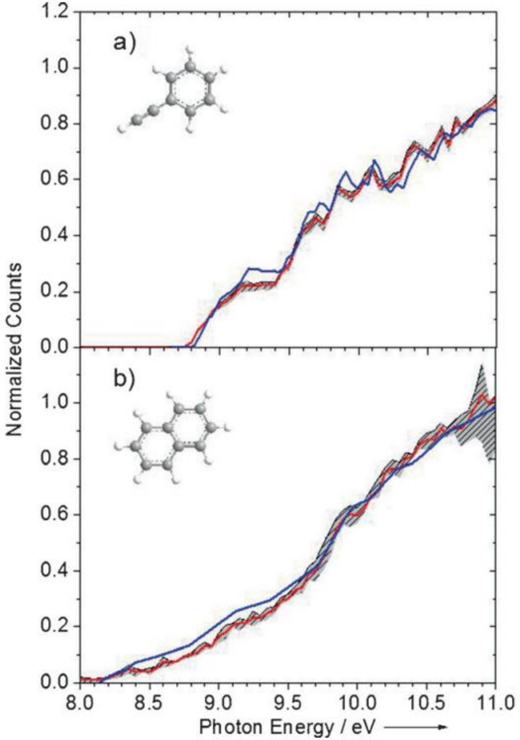
GAS PHASE CHEMICAL PHYSICS

A. M. Mebel, Y. Georgievskii, A. W. Jasper, S. J. Klippenstein, “Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene”, *Proc. Combust. Inst.*, **2017,** 36, 919-926

The HACA Mechanism

H-Abstraction-C_2H_2-Addition





Pyrolysis/reactor experiment:
Phenyl + acetylene

$$C_6H_5^{\bullet} + C_2H_2 \rightarrow C_8H_7^{\bullet}$$

$$C_8H_7^{\bullet} \rightarrow C_8H_6 + H^{\bullet}$$

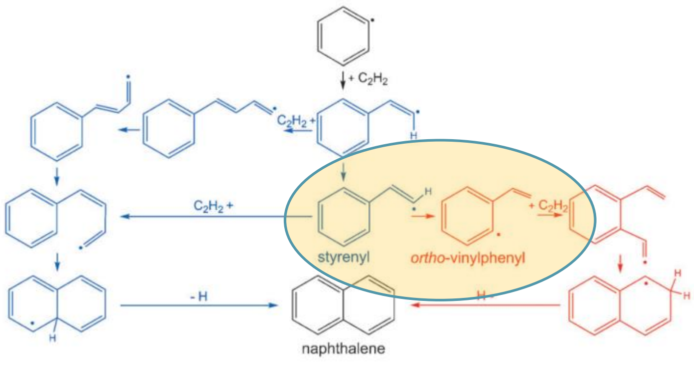
$$C_8H_7^{\bullet} + C_2H_2 \rightarrow C_{10}H_9^{\bullet}$$

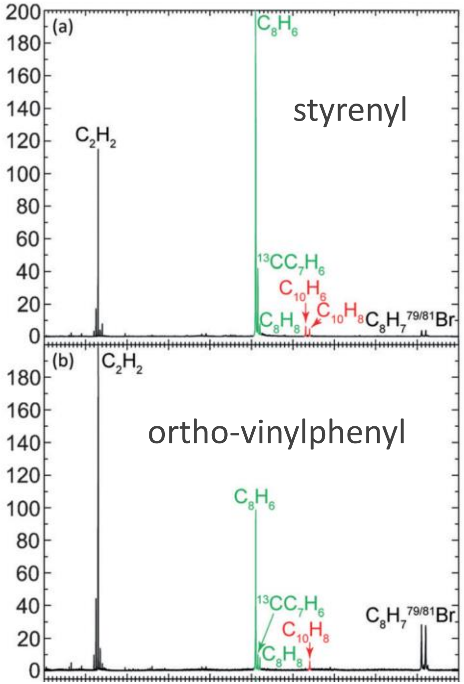
$$C_{10}H_9^{\bullet} \rightarrow C_{10}H_8 + H^{\bullet}$$

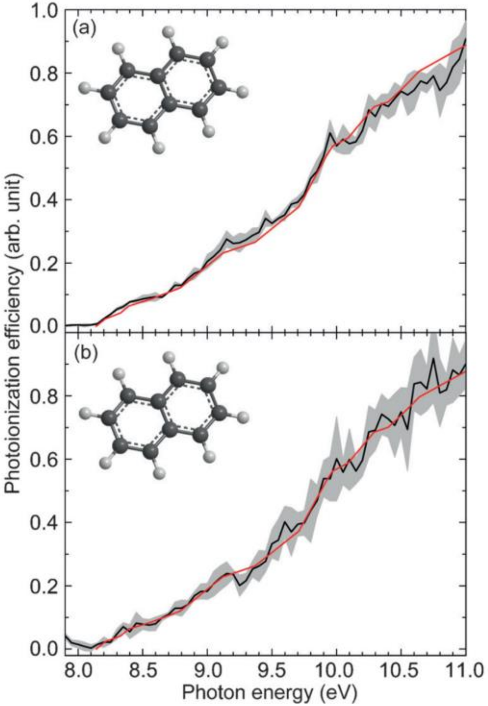
D. S. N. Parker, R. I. Kaiser, T. P. Troy, M. Ahmed, “Hydrogen Abstraction/Acetylene Addition Revealed”, *Angew. Chem. Int. Ed.*, **2014,** 53, 7740 –7744

The HACA Mechanism

H-Abstraction-C_2H_2-Addition







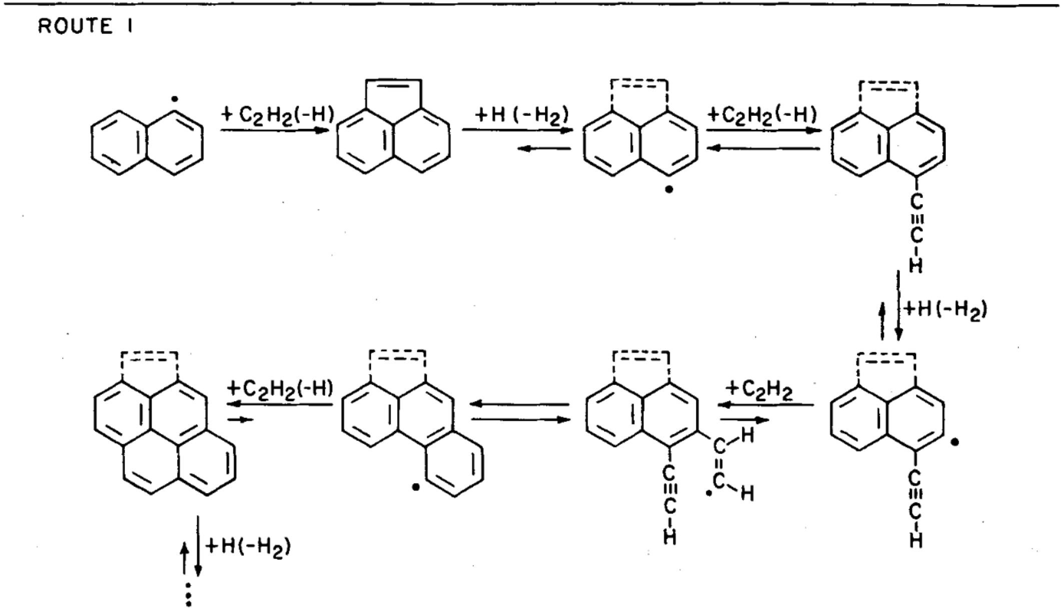
m/z =126: diethynylbenzene

T. Yang, T. P. Troy, B. Xu, O. Kostko, M. Ahmed, A. M. Mebel, R. I. Kaiser, “Hydrogen-Abstraction/Acetylene-Addition Exposed”, *Angew. Chem. Int. Ed.*, **2016,** 55, 14983 –14987

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

Further Growth of Fused Polycyclic Aromatics

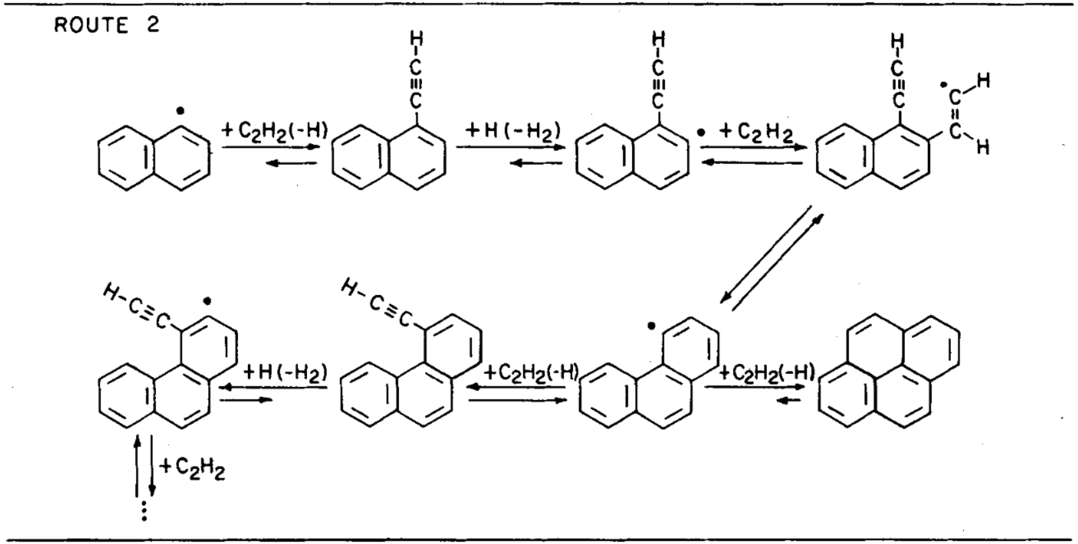


M. Frenklach *et al.*, “Detailed Kinetic Modeling of Soot Formation in Shock-Tube Pyrolysis of Acetylene”, *Proc. Combust. Inst.*, **1984,** 20, 887-901

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

Further Growth of Fused Polycyclic Aromatics



M. Frenklach *et al.*, “Detailed Kinetic Modeling of Soot Formation in Shock-Tube Pyrolysis of Acetylene”, *Proc. Combust. Inst.*, **1984,** 20, 887-901

The HACA Mechanism

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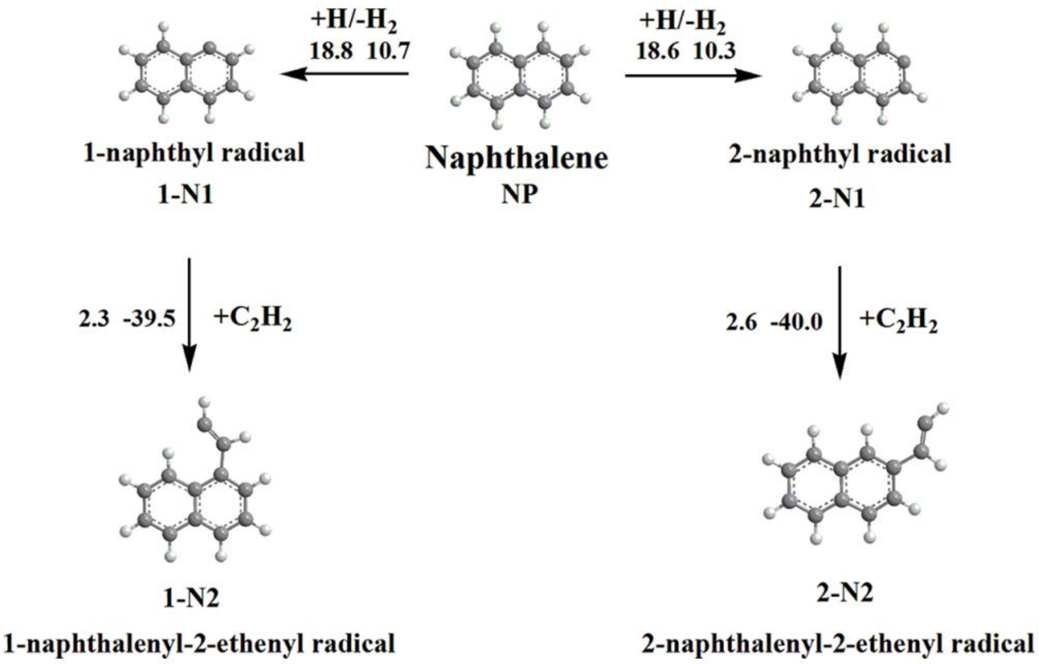
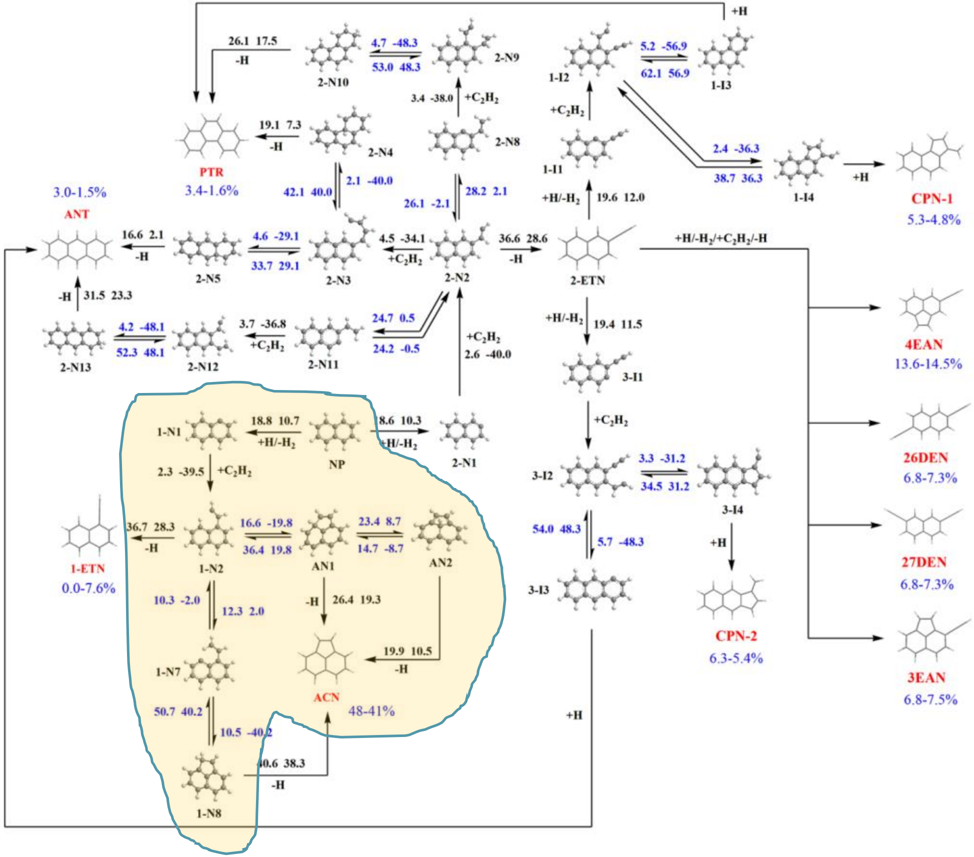


V. V. Kislov, A. I. Sadovnikov, A. M. Mebel, "Formation Mechanism of Polycyclic Aromatic Hydrocarbons beyond the Second Aromatic Ring", *J. Phys. Chem. A,* **2013,** 117, 4794-4816

The HACA Mechanism

H-Abstraction-C_2H_2-Addition

- Acetylene addition to the radical site at a carbon atom adjacent to the bay region of naphthalene or another similar PAH is highly unlikely to be followed by the addition of a second acetylene molecule.
- Instead, the closure of a bay region and buildup of an additional five-member ring occurs predominantly, following a hydrogen atom shift from the aromatic ring to the ethenyl group.
- For naphthalene, acetylene addition to 1-naphthyl radical produces acenaphthalene as the dominant reaction product accounting for consumption of 85–100% of the initial 1-naphthyl radical depending on temperature.
- Another product, 1-ethenylnaphthalene, is minor and appears only at high temperatures, beyond the normal temperature regime in most combustion flames.



V. V. Kislov, A. I. Sadovnikov, A. M. Mebel, “Formation Mechanism of Polycyclic Aromatic Hydrocarbons beyond the Second Aromatic Ring”, *J. Phys. Chem. A,* **2013,** 117, 4794-4816

The HACA Mechanism

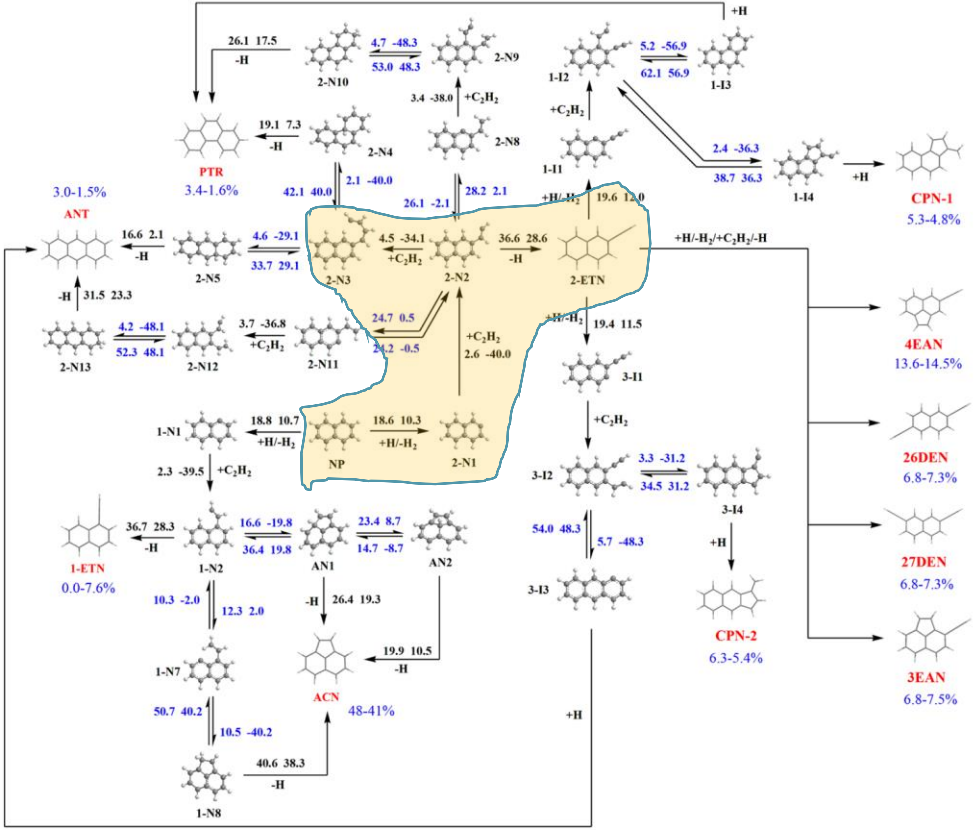
H-Abstraction-C_2H_2-Addition

- When a first acetylene molecule adds to a carbon atom in PAH not adjacent to the bay region (e.g., 2-naphthyl radical), both single-activation mechanisms involving second acetylene additions to the side chain or to the aromatic ring after its activation by internal hydrogen abstraction, which may lead to the buildup of an additional six-member ring, are not competitive.

- For naphthalene, the higher PAHs, anthracene
- and phenanthrene, are not produced at T =1000–2000 K.

- Instead, hydrogen atom elimination from the attached ethenyl group takes place, resulting in the formation of the initial PAH substituted with the ethynyl group, such as 2-ethynylnaphthalene

- A buildup of an additional six-member ring can only take place at temperatures below 1000 K.



V. V. Kislov, A. I. Sadovnikov, A. M. Mebel, “Formation Mechanism of Polycyclic Aromatic Hydrocarbons beyond the Second Aromatic Ring”, *J. Phys. Chem. A,* **2013,** 117, 4794-4816

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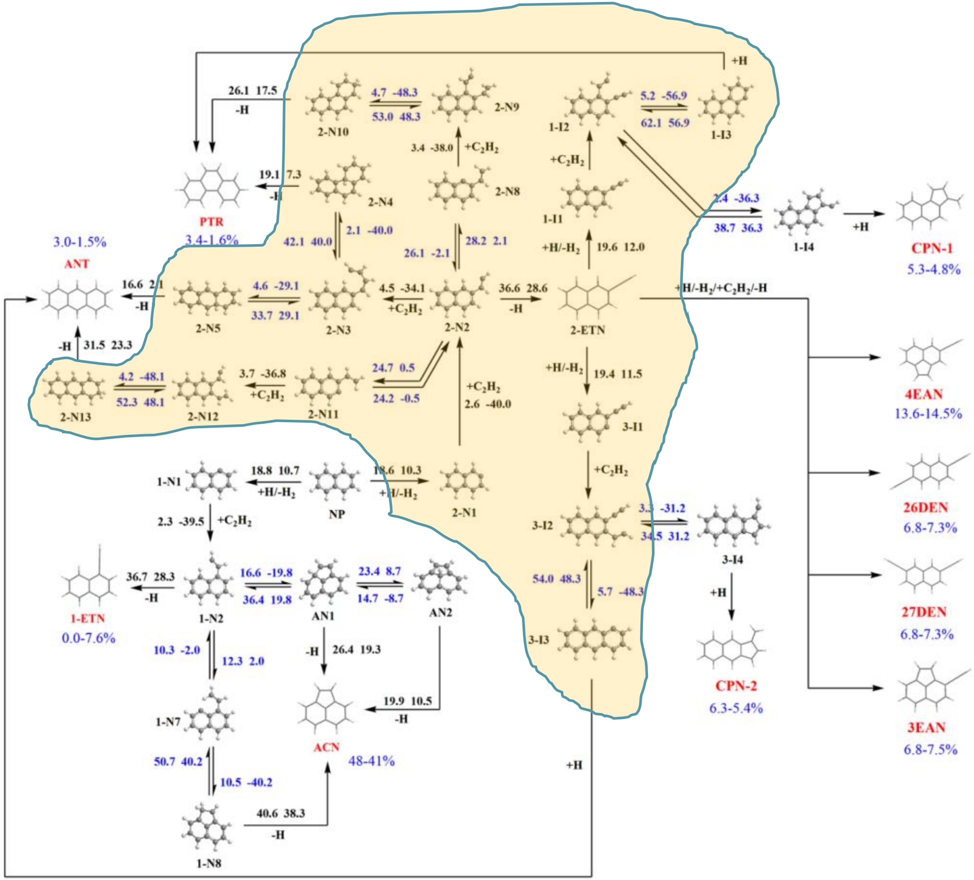
The HACA Mechanism

H-Abstraction-C_2H_2-Addition

- The formation of an additional six-member ring may occur only after intermolecular hydrogen abstraction from ethynyl-substituted PAH formed at the first stage, i.e., after addition of the first acetylene followed by H-elimination from the ethenyl group.
- Such H-abstraction must involve carbon atoms adjacent to the existing ethynyl (C_2H) fragment producing PAH structure with two adjacent ethynyl and ethenyl groups.
- These groups may subsequently undergo a fast closure of a new six-member ring.
- The formation of a new six-member ring via this mechanism can account only for ~25% of the total product yield, whereas the remaining ~75% of the products are cyclopentafused PAH.



V. V. Kislov, A. I. Sadovnikov, A. M. Mebel, “Formation Mechanism of Polycyclic Aromatic Hydrocarbons beyond the Second Aromatic Ring”, *J. Phys. Chem. A,* **2013,** 117, 4794-4816

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Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

Lecture 4: Napthalene Formation

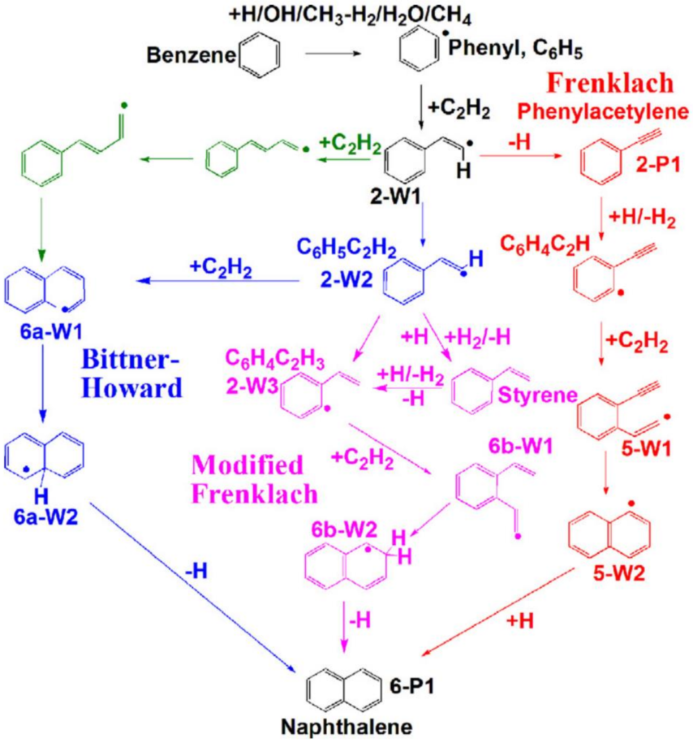
Nils Hansen

Sandia National Laboratories

Naphthalene Formation

H-Abstraction-C_2H_2-Addition

What other pathways, beyond HACA, can contribute to naphthalene formation?



A. M. Mebel, Y. Georgievskii, A. W. Jasper, S. J. Klippenstein, “Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene”, *Proc. Combust. Inst.,* **2017,** 36, 919-926

Naphthalene Formation

Beyond HACA

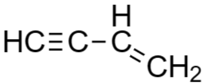
Cyclopentadienyl Reactions:

$C_5H_5 + C_5H_5$

Phenyl/Benzene Reactions:

C_6H_5 + *i*-C_4H_3

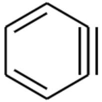
$C_6H_5 + C_4H_4$ (vinylacetylene)



$HC\equiv C-\overset{H}{C}=CH_2$

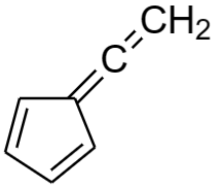
C_6H_5 + *i*-C_4H_5

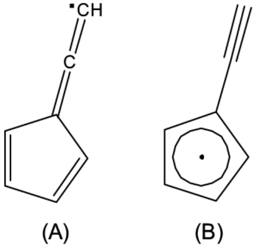
C_6H_6 + *o*-C_6H_4 (*o*-benzyne)



Fulvenallene/Fulvenallenyl Reactions:

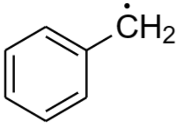
$C_5H_4CCH_2/C_5H_4CCH + C_3H_3$ (propargyl)





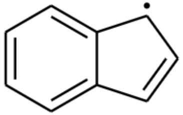
Benzyl Reactions:

$C_7H_7 + C_3H_3$ (propargyl)

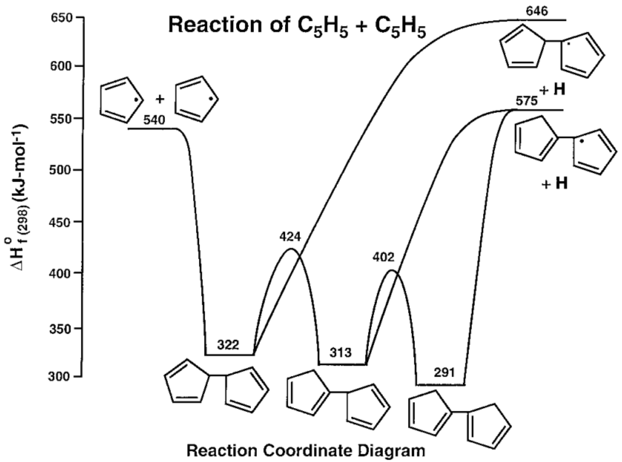


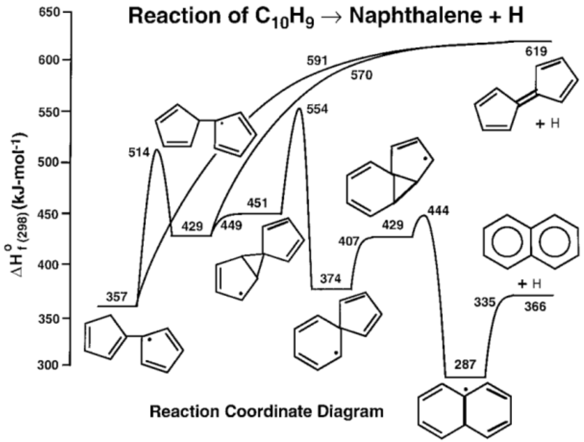
Indenyl Reactions:

$C_9H_7 + CH_3$ (methyl)

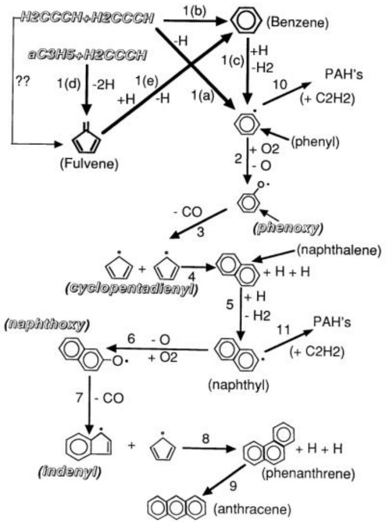


$C_5H_5 + C_5H_5$





Melius *et al.,* “Reaction Mechanisms in Aromatic Hydrocarbon Formation Involving the C5H5 Cyclopentadienyl Moiety”, *Proc. Combst. Inst.,* **1996,** 26, 685-692



Marinov et al., “Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Laminar Premixed n-Butane Flame”, *Combust. Flame,* **1998,** 114(1-2), 192-213

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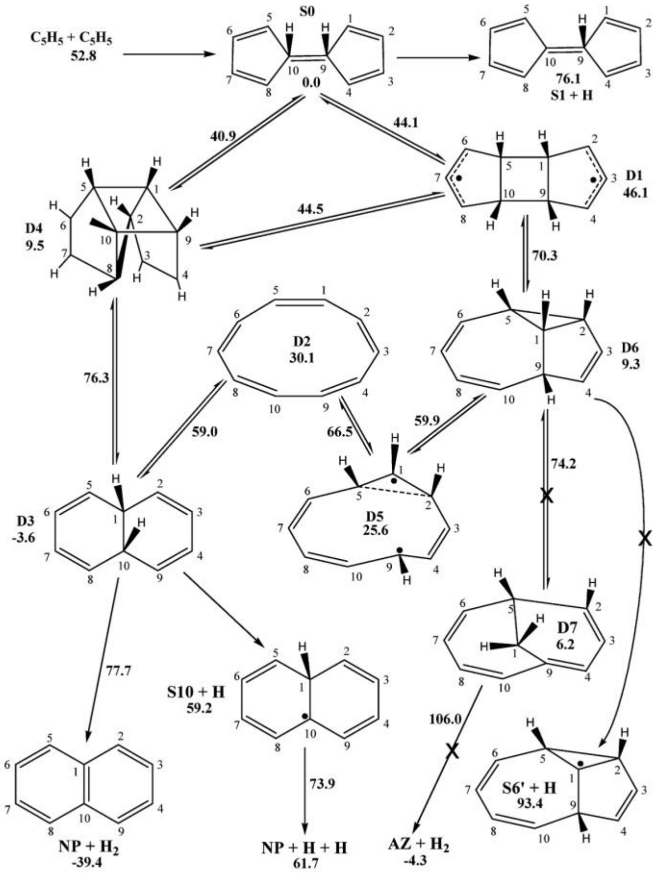
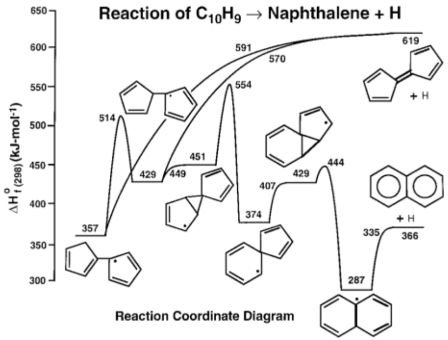
$C_5H_5 + C_5H_5$

- naphthalene can be produced from the recombination of two cyclopentadienyl radicals and is expected to be a favorable product of this reaction sequence at T < 1000 K
- Naphthalene would be formed through isomerizations and H atom loss on the C10H9 PES (after the initial H elimination from C10H10) and not in conjunction with molecular hydrogen.

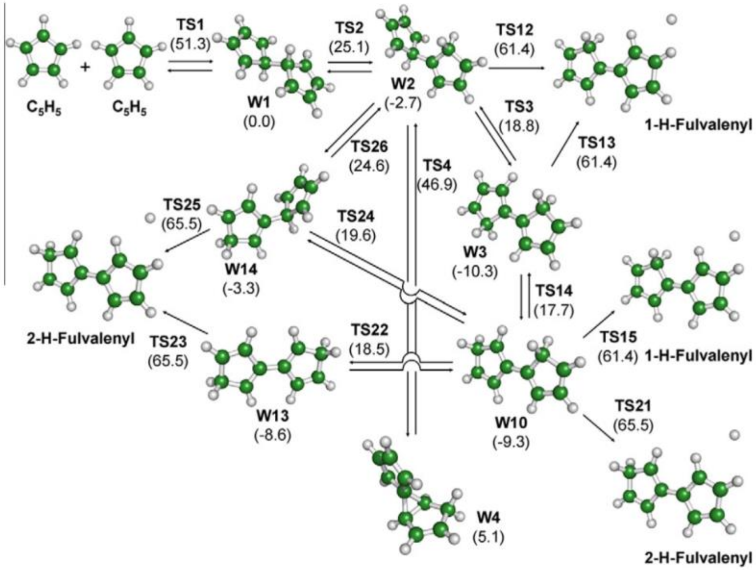


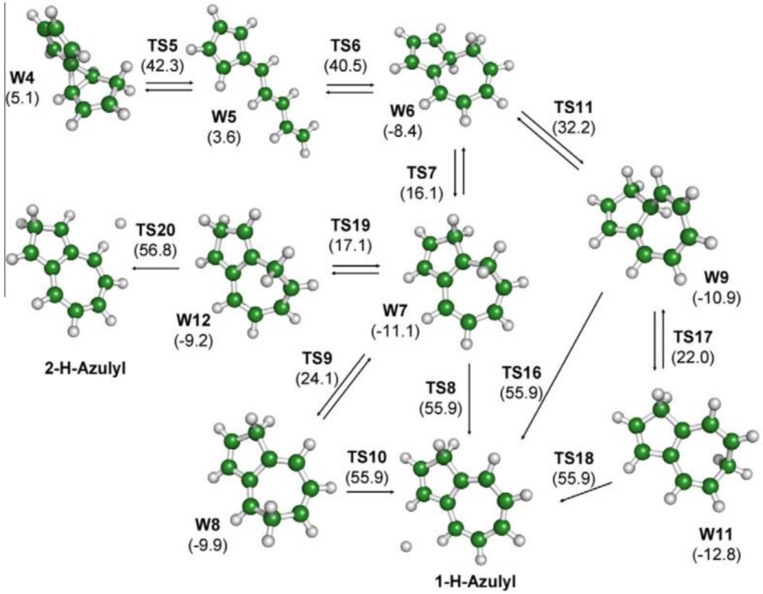


A. M. Mebel and V. V. Kislov, “Can the C5H5 + C5H5 = C10H10 = C10H9+H/C10H8+H2 Reaction Produce Naphthalene? An Ab Initio/RRKM Study”, *J. Phys Chem. A,* **2009,** 113, 9825-9833

$C_5H_5 + C_5H_5$

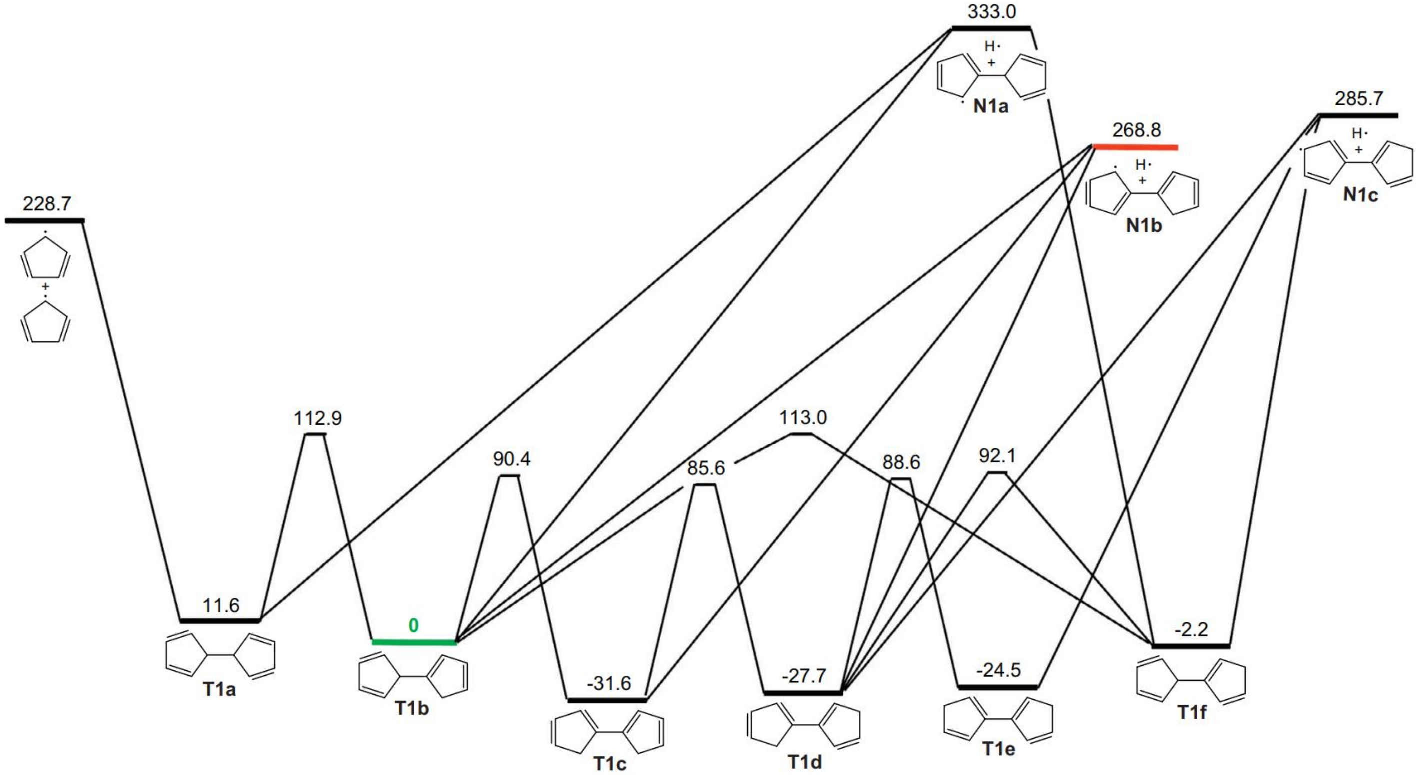
- ➢ The mechanism is characterized by a beta-opening reaction, facilitated by a stabilization effect due to conjugation, and by the formation of azulyl radicals as reaction products
- ➢ As known, the conversion of azulyl to naphthalene is a relatively fast process, so that the mechanism here proposed is an effective route for the formation of naphthalene





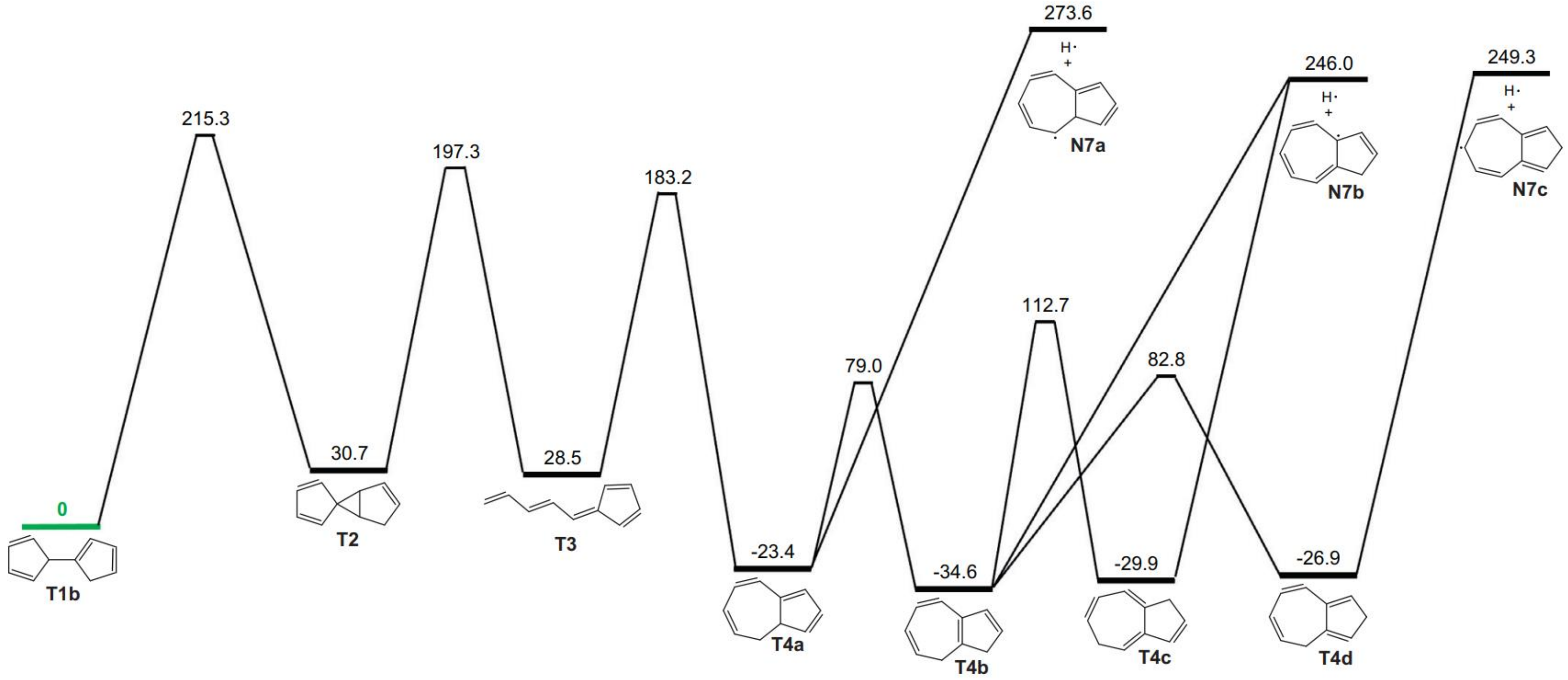
C. Cavallotti and D. Polino, “On the kinetics of the C5H5 + C5H5 reaction”, *Proc. Combust. Inst.,* **2013,** 34, 557-564

$C_5H_5 + C_5H_5$



A. E. Long *et al.*, “Pressure dependent kinetic analysis of pathways to naphthalene from cyclopentadienyl recombination”, *Combust Flame,* **2018,** 187, 247-256

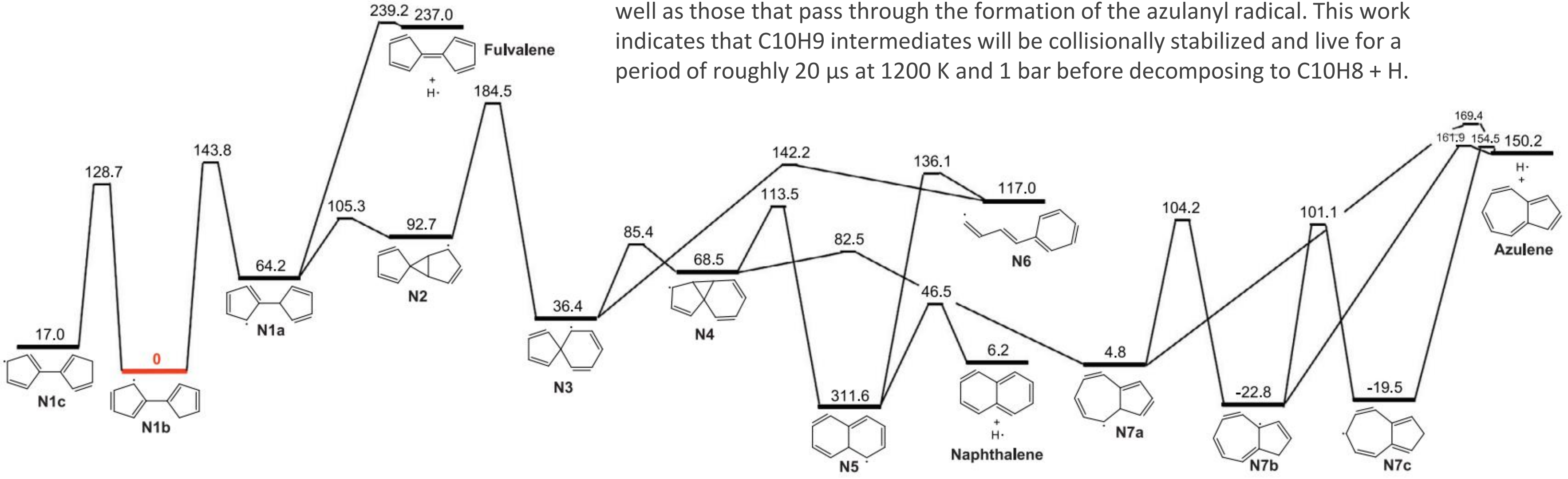
$C_5H_5 + C_5H_5$



A. E. Long *et al.*, "Pressure dependent kinetic analysis of pathways to naphthalene from cyclopentadienyl recombination", *Combust Flame,* **2018,** 187, 247-256

$C_5H_5 + C_5H_5$

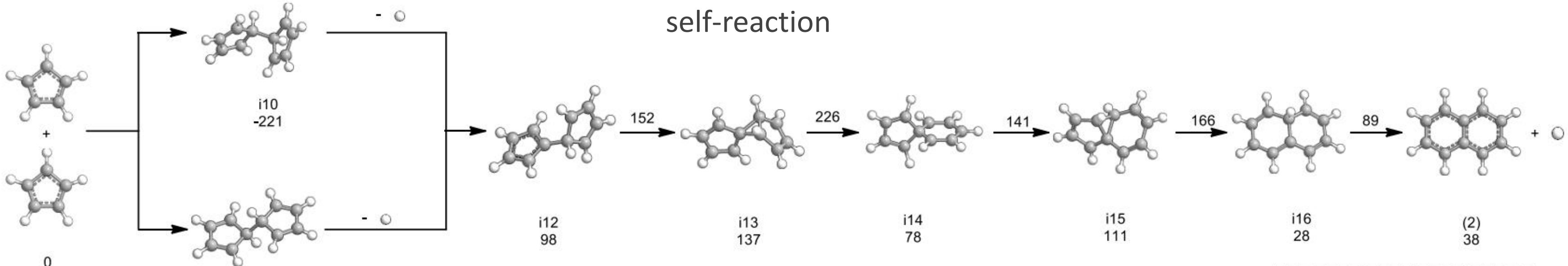
- naphthalene is mainly formed via a series of reaction steps starting with the formation of C10H10 isomers and not through the direct chemically activated reaction C5H5 + C5H5 → C10H8 + H + H
- since C–H scission of any C10H10 isomer is highly endothermic, the C10H10 species are predicted to accumulate to high concentrations which enable bimolecular hydrogen abstraction reactions to become competitive.
- Isomerizations on the C10H9 surface directly to naphthalene are considered as well as those that pass through the formation of the azulanyl radical. This work indicates that C10H9 intermediates will be collisionally stabilized and live for a period of roughly 20 µs at 1200 K and 1 bar before decomposing to C10H8 + H.

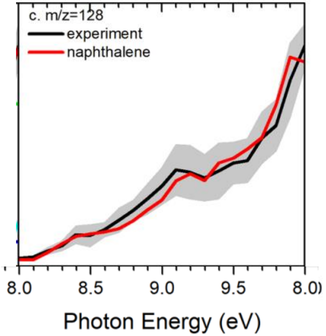


A. E. Long *et al.*, "Pressure dependent kinetic analysis of pathways to naphthalene from cyclopentadienyl recombination", *Combust Flame,* **2018,** 187, 247-256

$C_5H_5 + C_5H_5$

High-T reactor experiments provide compelling evidence for the formation of naphthalene through the cyclopentadienyl self-reaction

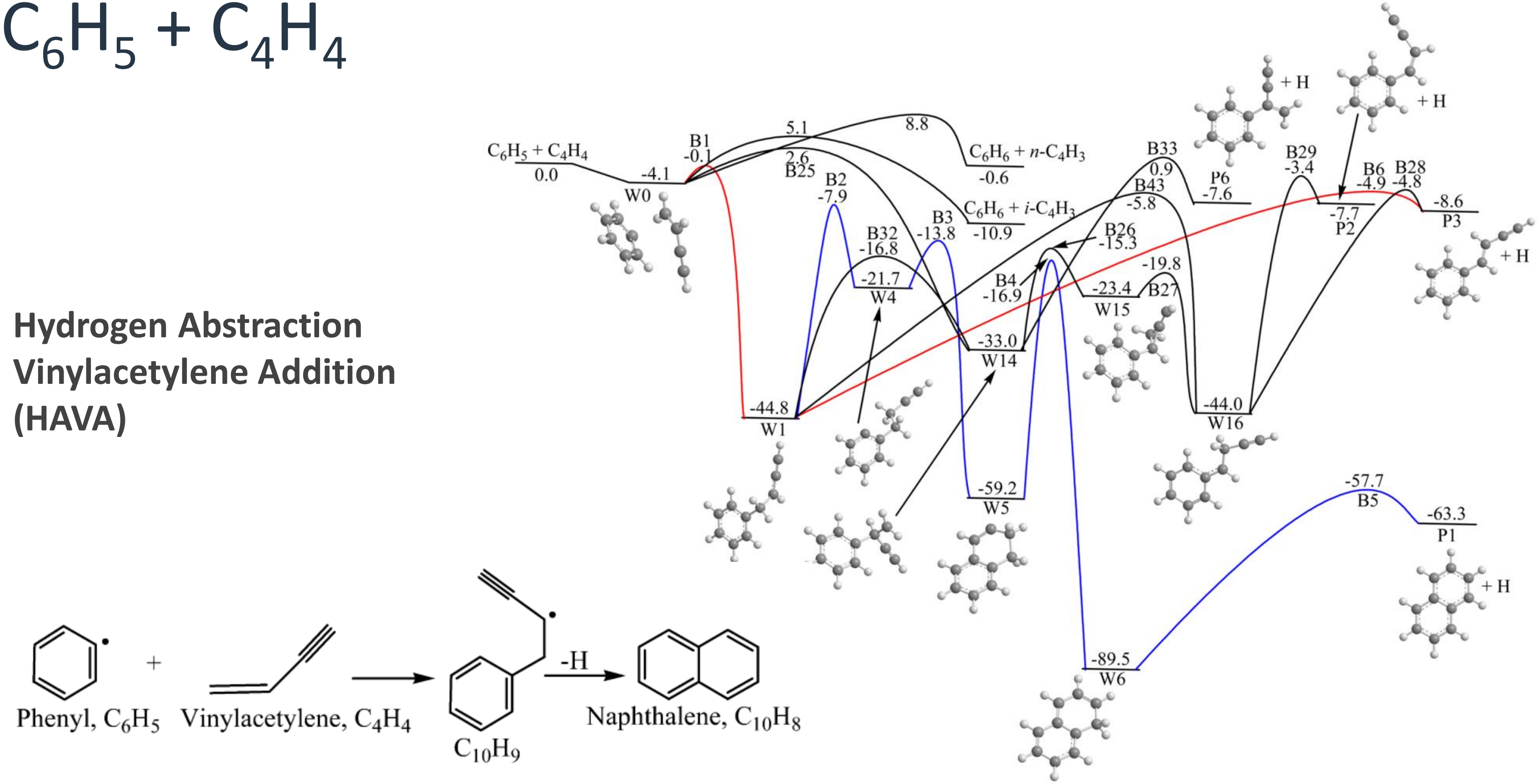




R. I. Kaiser *et al.*, “Formation of Benzene and Naphthalene through Cyclopentadienyl-Mediated Radical-Radical Reactions”, *J. Phys. Chem. Lett,* **2022,** 13, 208-213

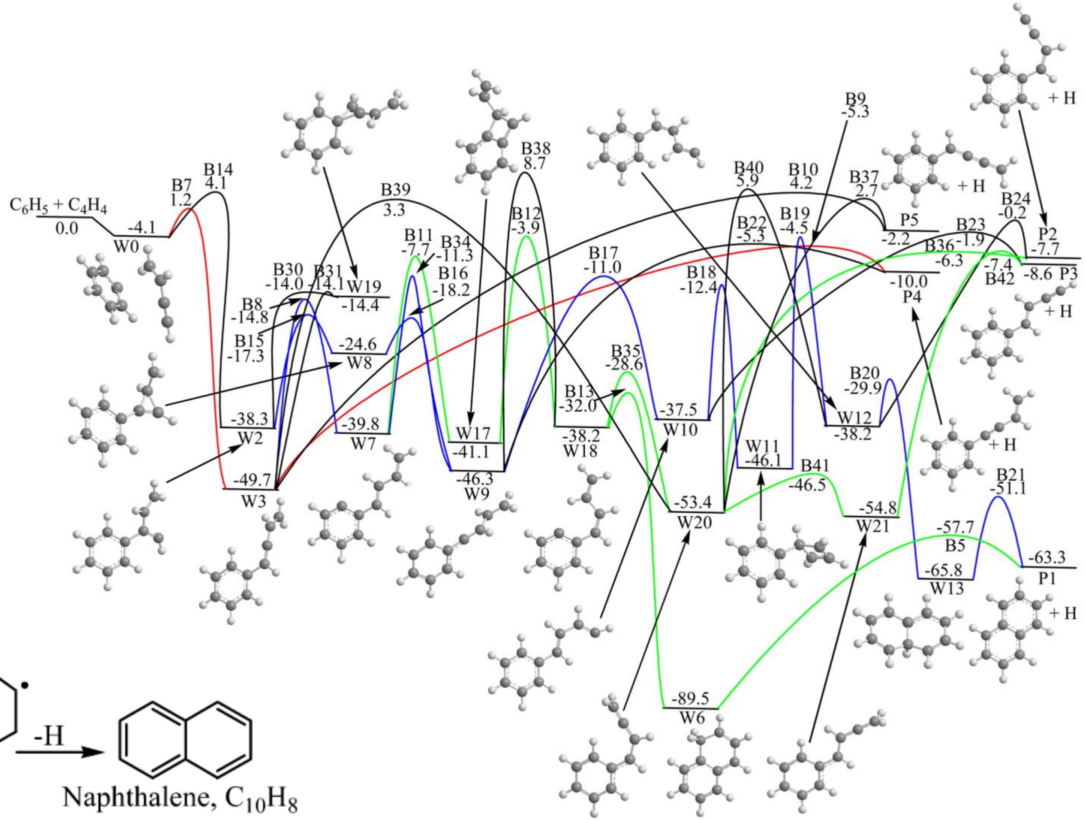
$C_6H_5 + C_4H_4$

Hydrogen Abstraction Vinylacetylene Addition (HAVA)

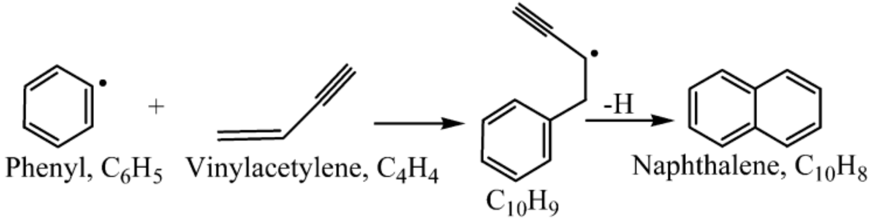


A. M. Mebel *et al.*, "Formation Mechanism of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames", *J. Phys. Chem. A,* **2017,** 121, 901-926

$C_6H_5 + C_4H_4$



Hydrogen Abstraction Vinylacetylene Addition (HAVA)



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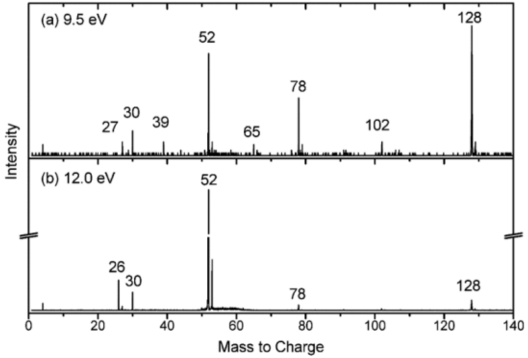
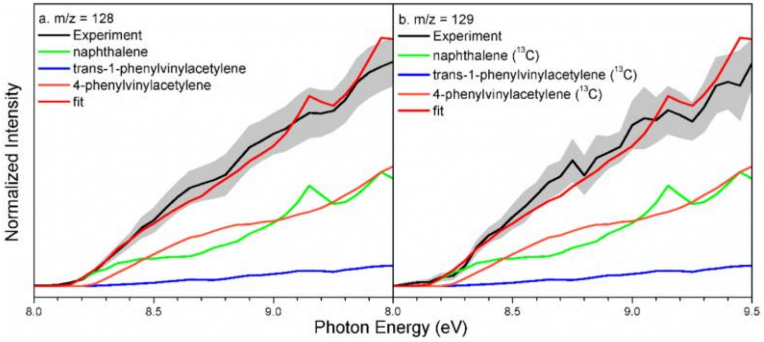
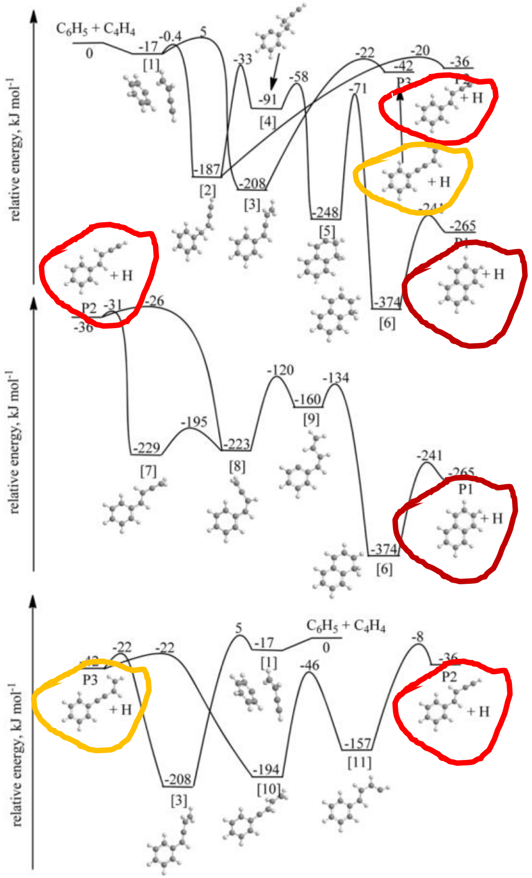
$C_6H_5 + C_4H_4$





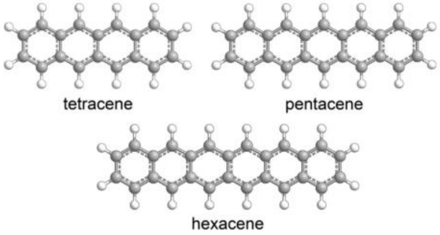


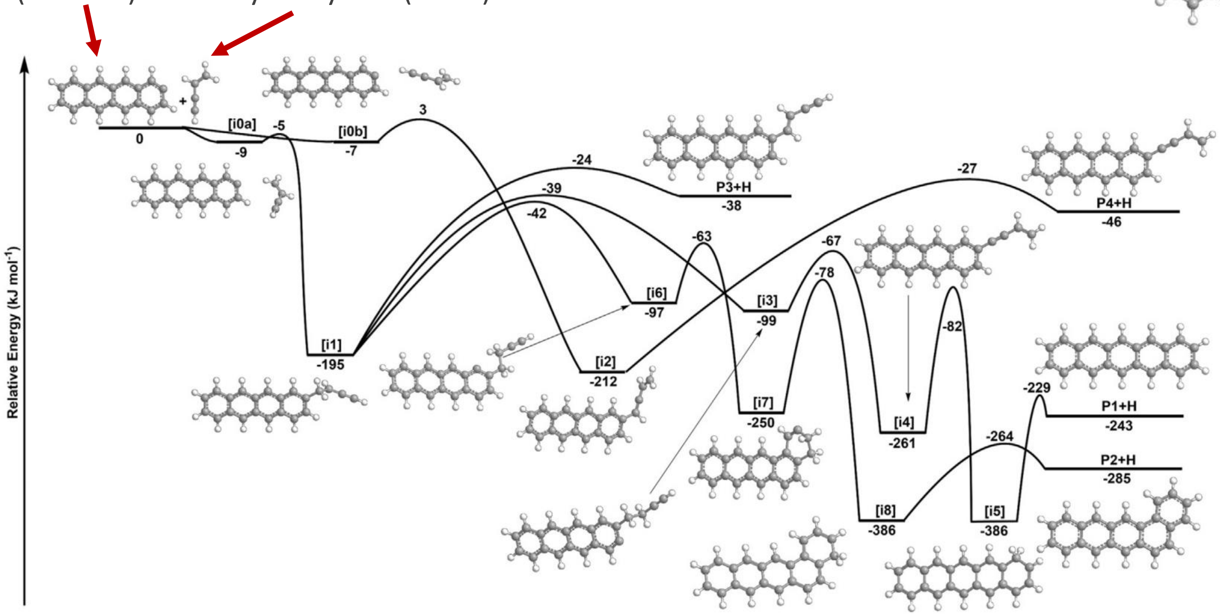
High-T reactor experiments provide compelling evidence for the formation of naphthalene through the HAVA (H-abstraction-Vinylacetylene Addition) mechanism.

L. Zhao *et al.*, “VUV Photoionization Study of the Formation of the Simplest Polycyclic Aromatic Hydrocarbon: Naphthalene (C10H8)”, *J. Phys. Chem. Lett.*, **2018,** 9, 2620-2626

$C_6H_5 + C_4H_4$

A representative, low- temperature gas-phase reaction mechanism synthesizing polyacenes via ring annulation exemplified by the formation of pentacene (C22H14) along with its benzo[a]tetracene isomer (C22H14) is unraveled by probing the elementary reaction of the 2-tetracenyl radical (C18H11) with vinylacetylene (C4H4).

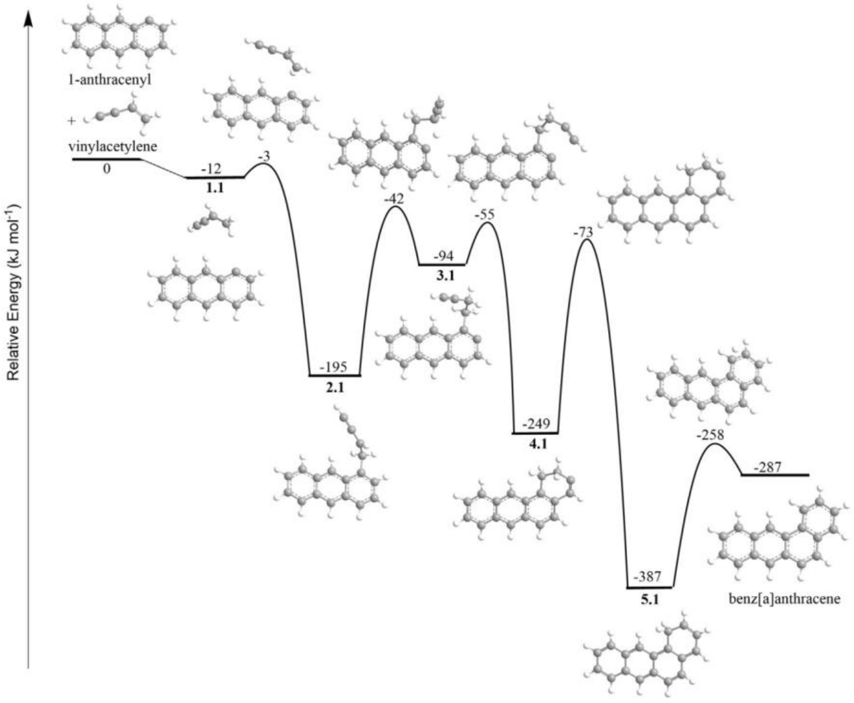




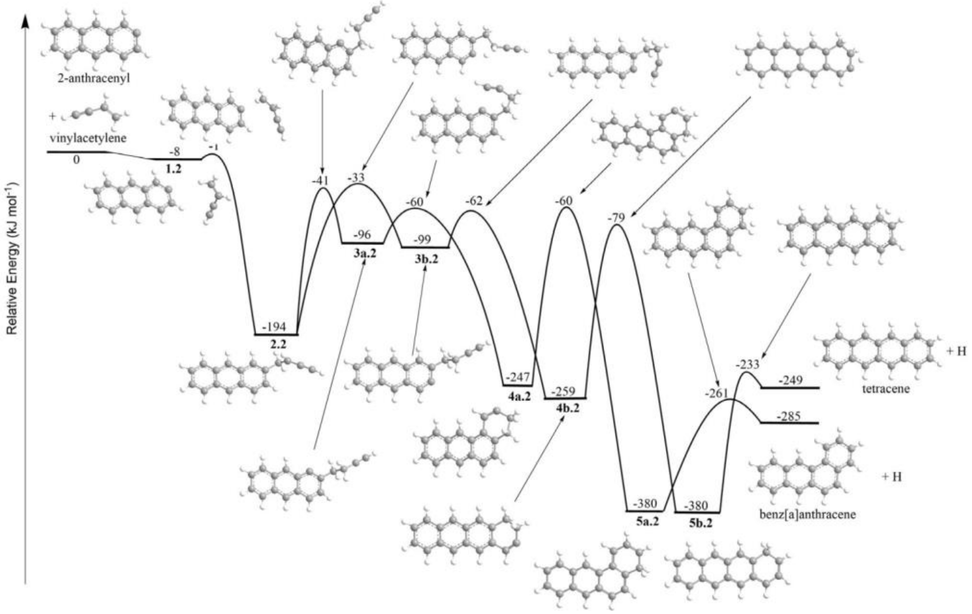
L. Zhao *et al.*, "A Free-Radical Prompted Barrierless Gas-Phase Synthesis of Pentacene", *Angew. Chem. Int. Ed.*, **2020,** 59, 11334-11338

$C_6H_5 + C_4H_4$

the hydrogen abstraction—vinylacetylene addition (HAVA) pathway signifies a versatile reaction mechanism to generate even more complex acenes, helicenes, and phenacenes through barrierless, stepwise ring expansion via elementary gas phase reactions of an aryl radical, which can be formed from the corresponding aromatic precursor via H-abstraction, with vinylacetylene



Acenes



L. Zhao *et al.*, "A Unified Mechanism on the Formation of Acenes, Helicenes, and Phenacenes in the Gas Phase", *Angew. Chem. Int. Ed.*, **2020,** 132, 4080-4087

$C_6H_5 + C_4H_4$

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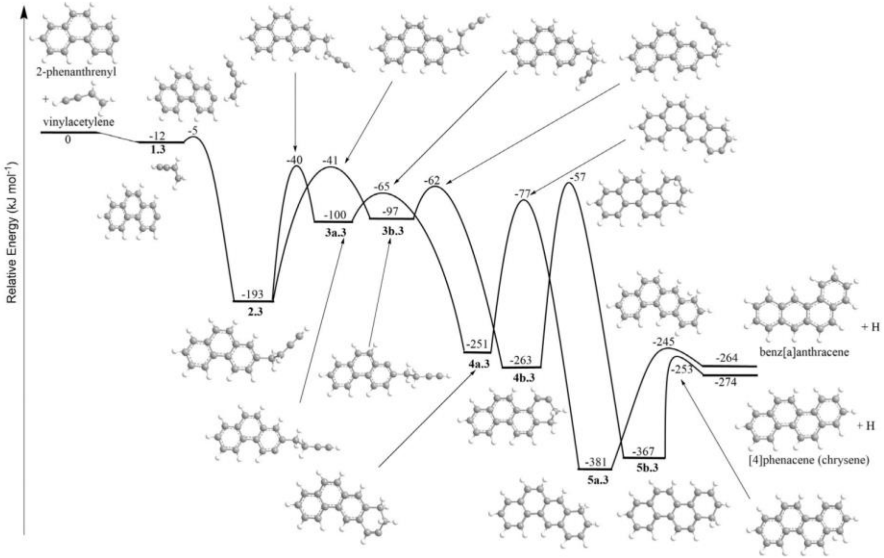
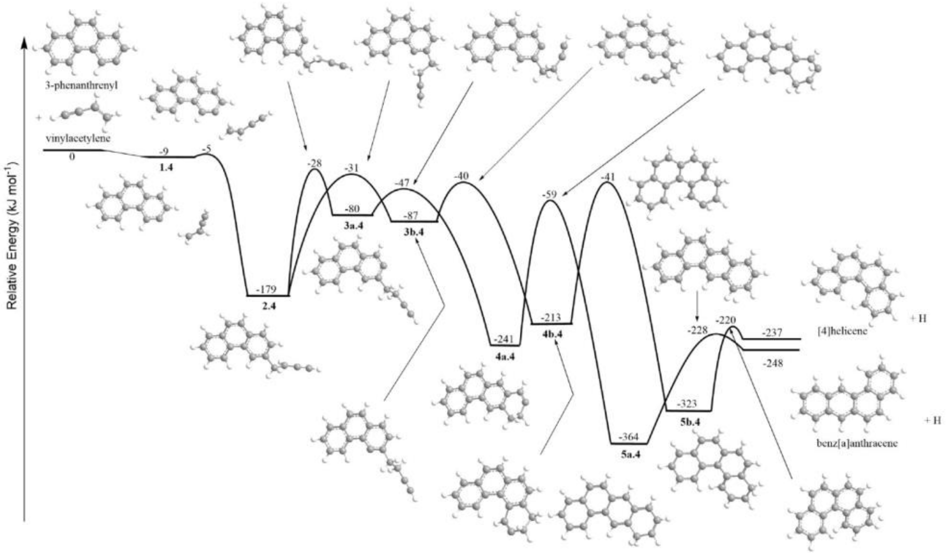
Phenacenes



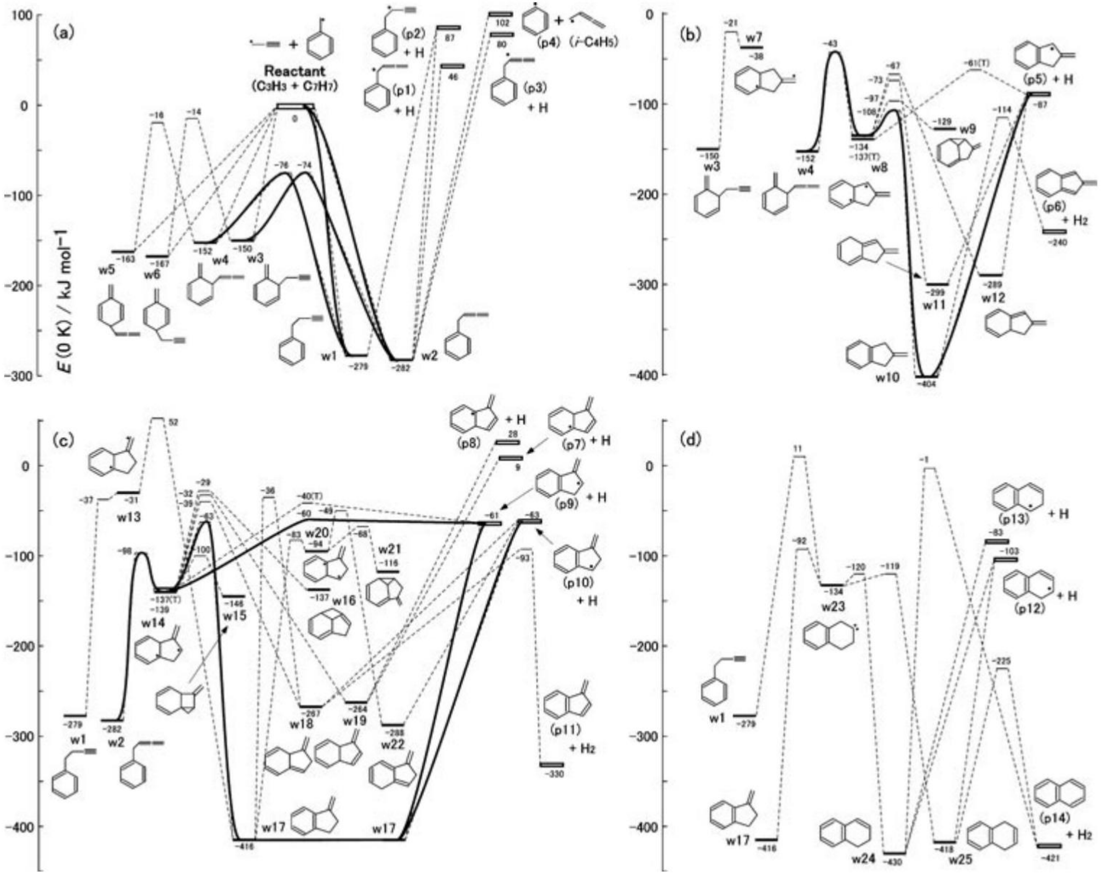
Helicenes



L. Zhao *et al.*, "A Unified Mechanism on the Formation of Acenes, Helicenes, and Phenacenes in the Gas Phase", *Angew. Chem. Int. Ed.*, **2020,** 132, 4080-4087

$C_7H_7 + C_3H_3$

- it was found that the reaction dominantly proceeds by the addition of the propargyl radical to the alpha(CH2) site of the benzyl radical
- the additions to the ortho- and the para-sites are unfavorable due to the loss of the aromaticity.



A. Matsugi and A. Miyoshi, “Computational study on the recombination reaction between benzyl and propargyl radicals”, *Int. J. Chem. Kin.*, **2012,** 44, 206-218

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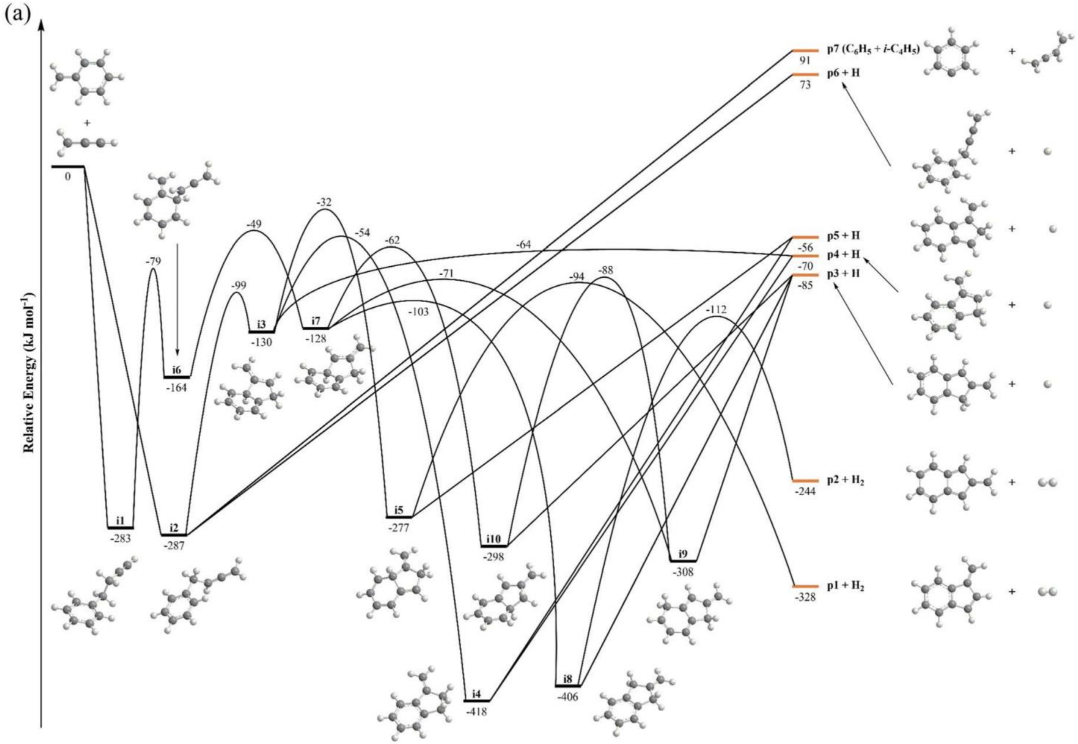
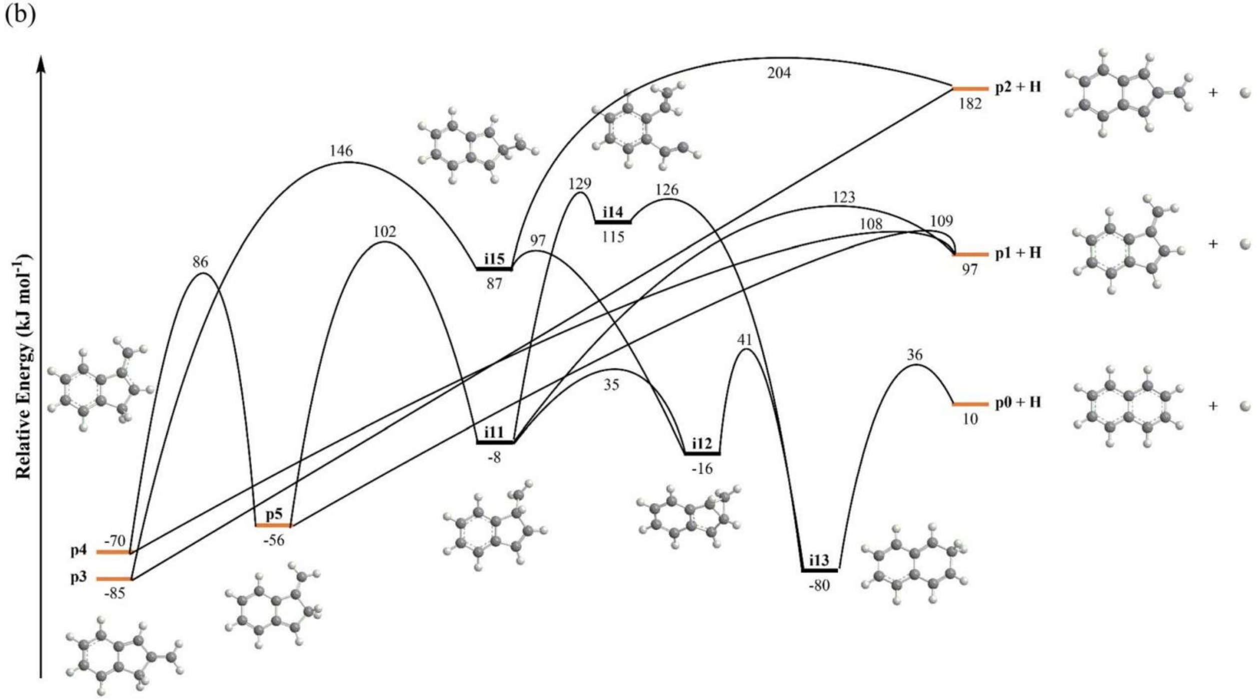
$C_7H_7 + C_3H_3$



C. He *et al.*, “Unconventional gas-phase preparation of the prototype polycyclic aromatic hydrocarbon naphthalene (C10H8) via the reaction of benzyl (C7H7) and propargyl (C3H3(radicals coupled with hydrogen-atom assisted isomerization”, *Chem. Sci.*, **2023,** 14, 5369

$C_7H_7 + C_3H_3$



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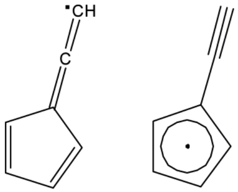
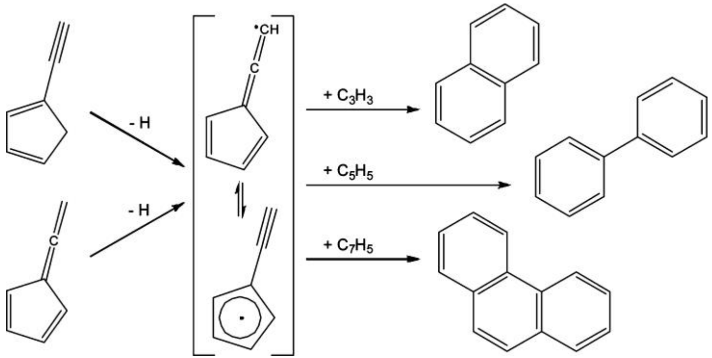
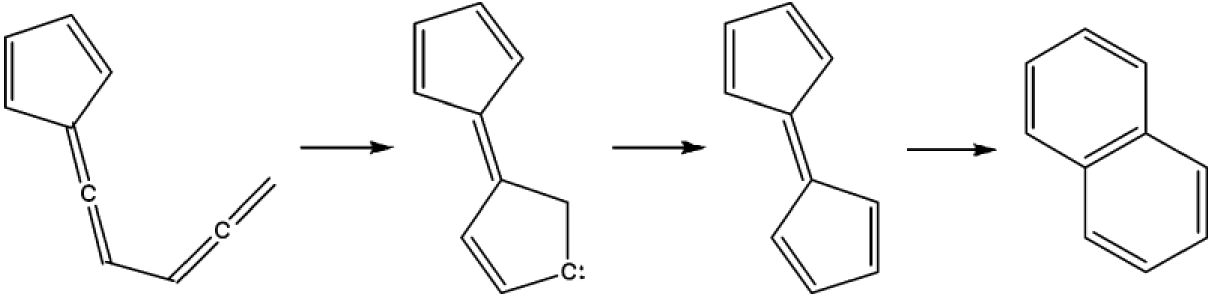
$C_7H_5 + C_3H_3$



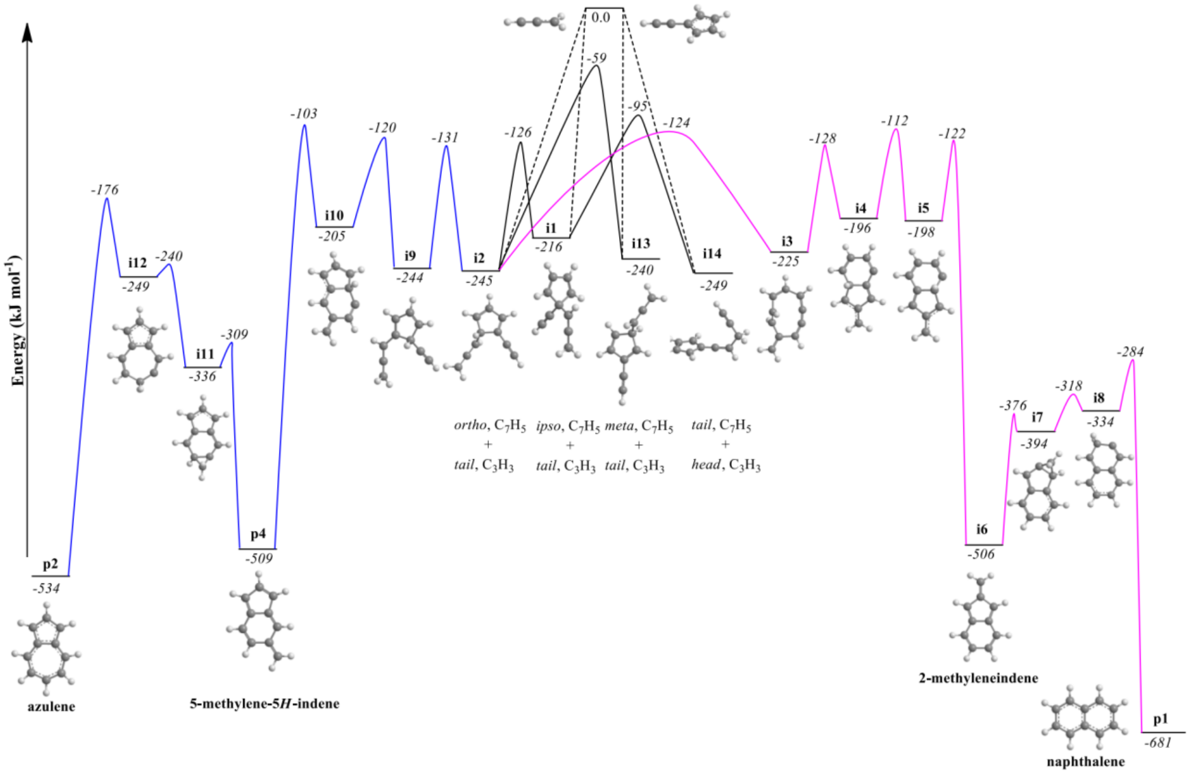
(A) (B)





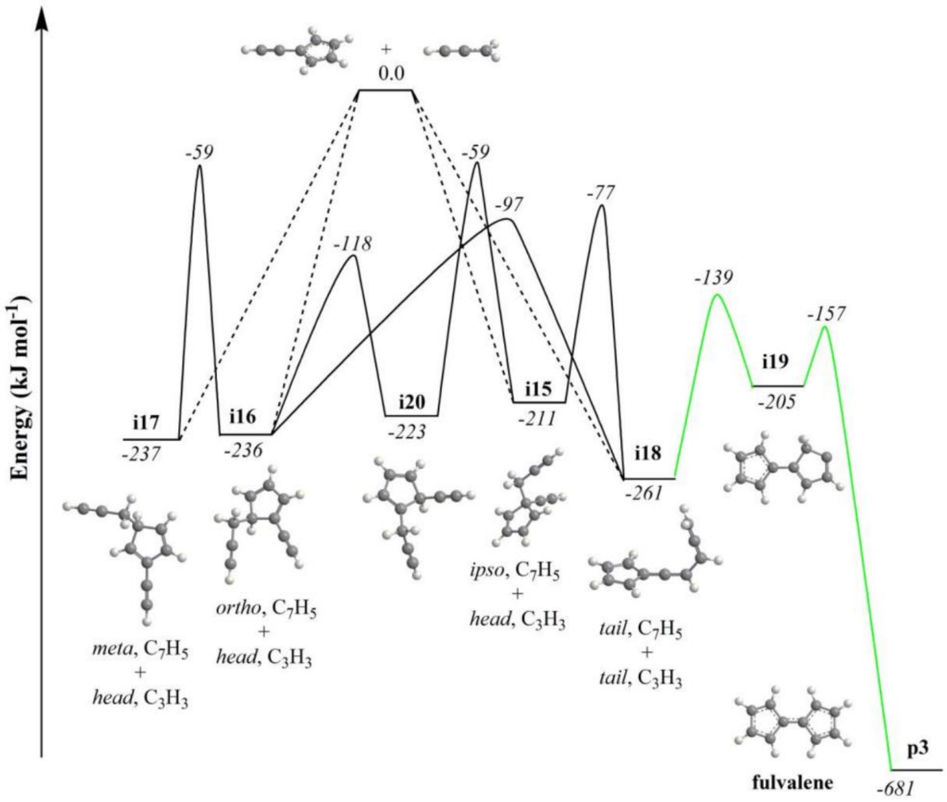
G. Da Silva and J. W. Bozzelli, "The C7H5 Fulvenallenyl Radical as a Combustion Intermediate: Potential New Pathways to Two- and Three-Ring PAHs", *J. Phys. Chem. Lett.*, **2009,** 113, 12045-12048

$C_7H_5 + C_3H_3$



W. Li *et al.*, "Gas-Phase Preparation of Azulene (C10H8) via Reaction of the Resonantly Stabilized Fulvenallenyl (C7H5•) and Propargyl (C3H3•) Radicals", *Chem. Sci.*, **2023,** submitted

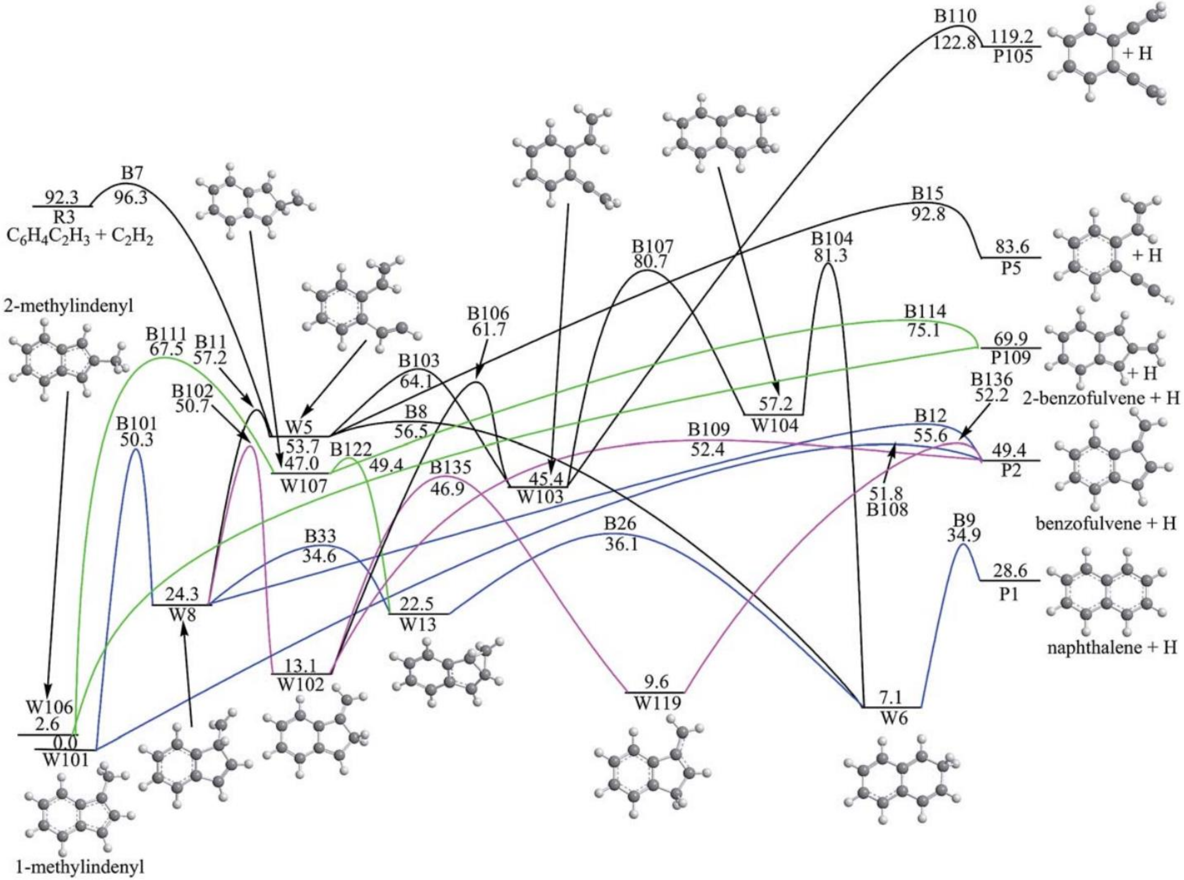
$C_7H_5 + C_3H_3$



W. Li *et al.*, “Gas-Phase Preparation of Azulene (C10H8) via Reaction of the Resonantly Stabilized Fulvenallenyl (C7H5•) and Propargyl (C3H3•) Radicals”, *Chem. Sci.*, **2023,** submitted

$C_9H_7 + CH_3$

- indene can be converted to benzofulvene or naphthalene under typical combustion conditions, via its activation by H atom abstraction and methyl substitution on the five-membered ring followed by isomerization and decomposition of the resulting 1-methylindenyl radical, C10H9 = C10H8 + H.
- Benzofulvene easily transforms to naphthalene by H-assisted isomerization



A. M. Mebel *et al.*, “Pressure-dependent rate constants for PAH growth: formation of indene and its conversion to naphthalene”, *Faraday Discuss.*, **2016,** 195, 637

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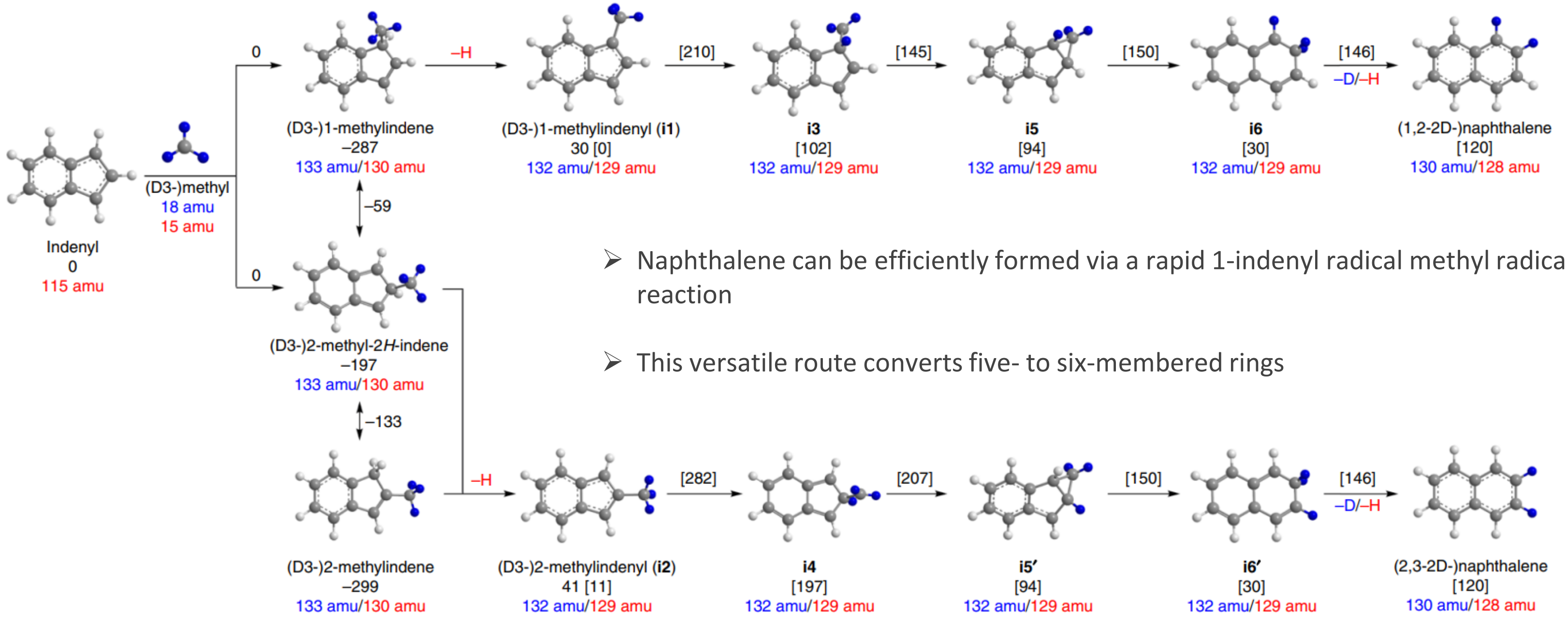
$C_9H_7 + CH_3$

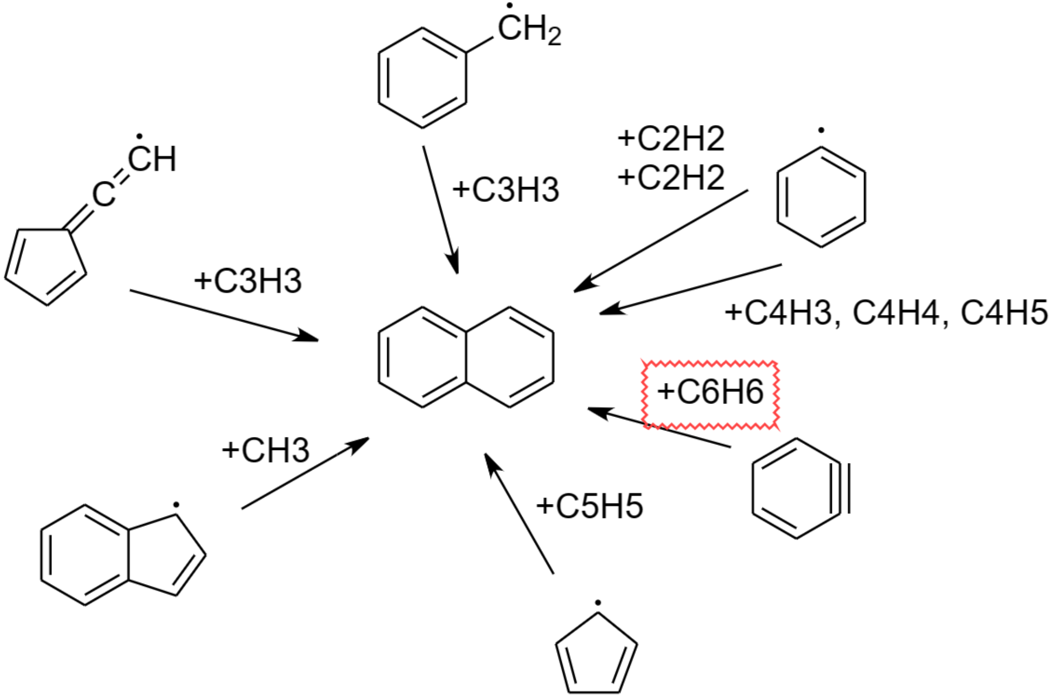
High-temperature reactor experiments confirm the formation of naphthalene



- Naphthalene can be efficiently formed via a rapid 1-indenyl radical methyl radical reaction
- This versatile route converts five- to six-membered rings

L. Zhao *et al.*, “Molecular mass growth through ring expansion in polycyclic aromatic hydrocarbons via radical-radical reactions”, *Nat. Com.*, **2019,** 10, 3689**,** https://doi.org/10.1038/s41467-019-11652-5

Naphthalene Formation - Summary



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Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

Lecture 5: Indene Formation

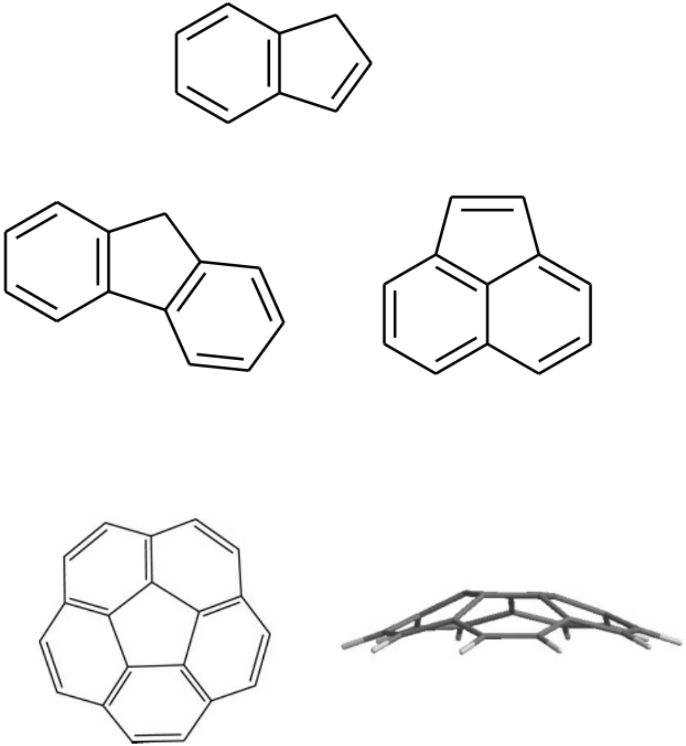
Sandia National Laboratories

Nils Hansen

COMBUSTION RESEARCH FACILITY
CRF
SANDIA NATIONAL LABORATORIES / CALIFORNIA

Indene Formation

- polycyclic aromatic hydrocarbons (PAH) containing both five- and six-membered rings are called cyclo-pentafused PAH, CP-PAH
- The simple CP-PAH species including indene, fluorene, acenaphthalene, etc., being abundant in flames, may be involved in further PAH growth producing nonplanar bowl-shaped structures like corannulene, which has been considered as a substructure and a possible precursor of fullerenes.



V. V. Kislov and A. M. Mebel, “Ab Initio G3-type Theory Study of the Formation of Indene in Combustion Flames. I. Pathways Involving Benzene and Phenyl Radical”, *J. Phys. Chem. A,* **2007,** 111, 3922-3931

Indene Formation

Cyclopentadienyl Pathway:

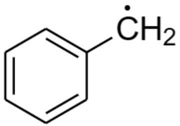
$C_5H_5 + C_4H_2$ (diacetylene)

Phenyl/Benzene Pathways:

$C_6H_5/C_6H_6 + C_3H_3$
$C_6H_5 + C_3H_4$ (allene/propyne)
$C_6H_5/C_6H_6 + C_3H_5$ (allyl)
$C_6H_5 + C_3H_6$ (propene)

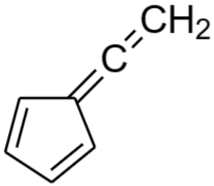
Benzyl Pathway:

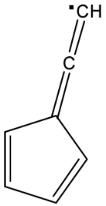
$C_6H_5CH_2 + C_2H_2$ (acetylene)



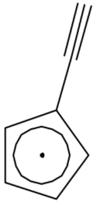
Fulvenallene/Fulvenallenyl Pathways:

$C_5H_4CCH_2/C_5H_4CCH + C_2H_2$(acetylene)





(A)

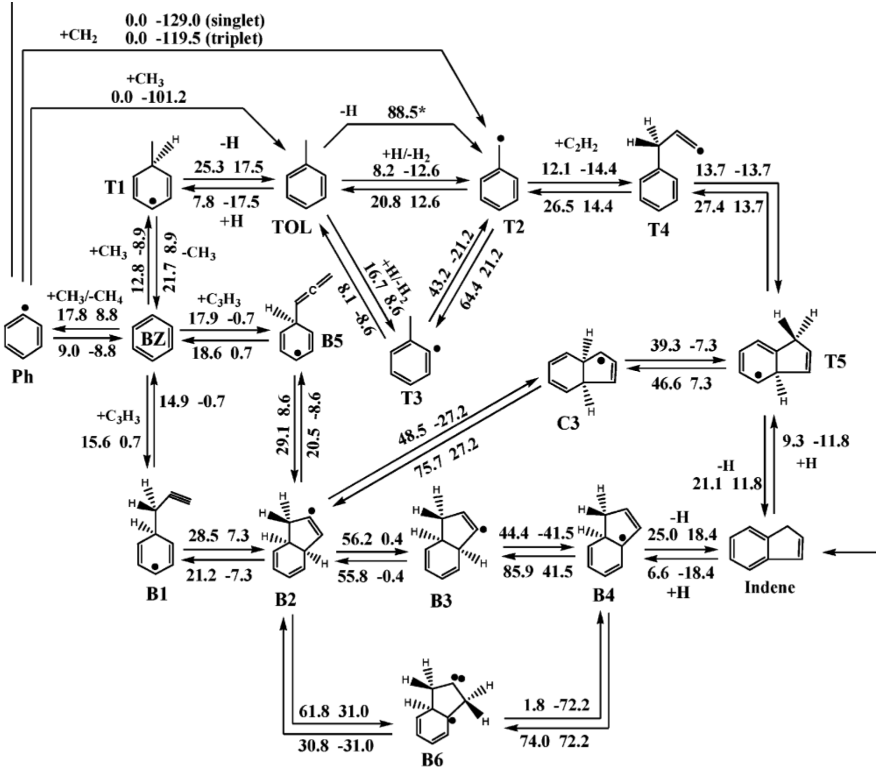


(B)

Phenylacetylene Pathway:

$C_8H_6 + CH_3$ (methyl)

$C_6H_{5/6} + C_3H_3$



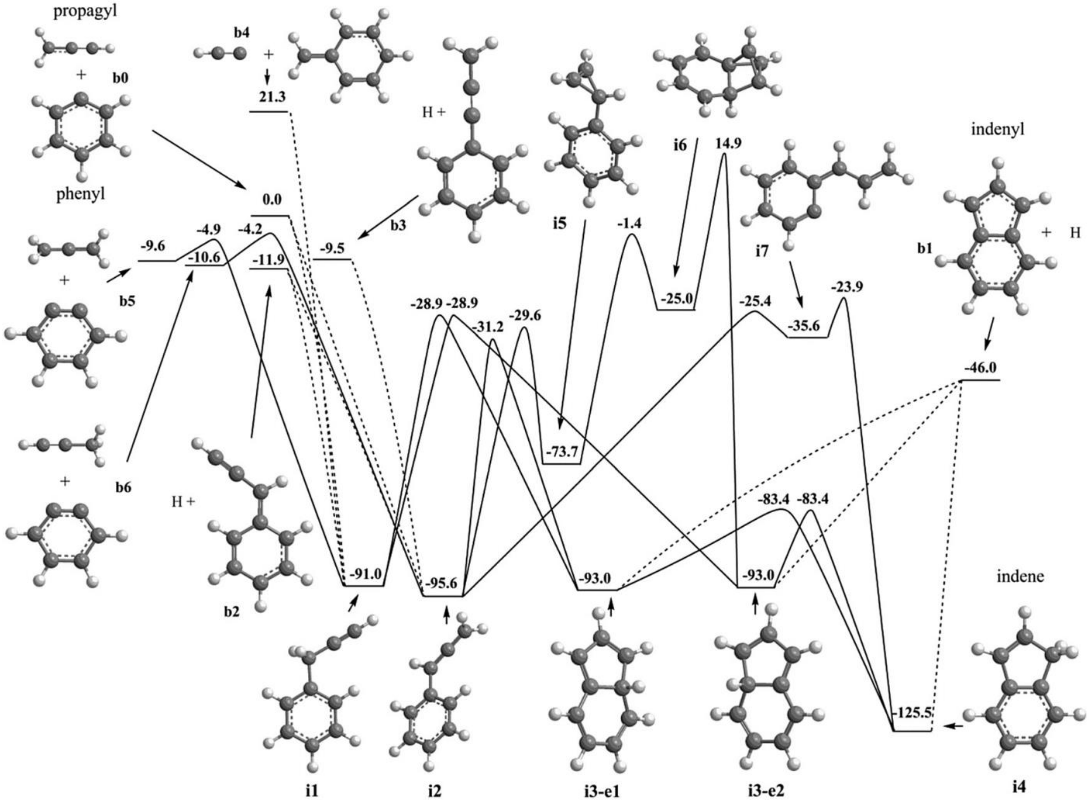
V. V. Kislov and A. M. Mebel, “Ab Initio G3-type/Statistical Theory Study of the Formation of Indene in Combustion Flames. I. Pathways Involving Benzene and Phenyl Radical”, *J. Phys Chem. A,* **2007,** 111, 3922-3931

$C_6H_5 + C_3H_3$

in the combustion relevant ranges of temperature and pressure, (T, p) = (500–2500 K, 30 Torr–100 atm), the following set of reactions should prove important in modeling the phenyl + propargyl association in hydrocarbon flames:

- phenyl + propargyl = indenyl + H
- phenyl + propargyl = 3-phenyl-1-propyne
- phenyl + propargyl = phenylallene
- phenyl + propargyl = C6H5CHCCH + H
- phenyl + propargyl = C6H5CCCH2 + H

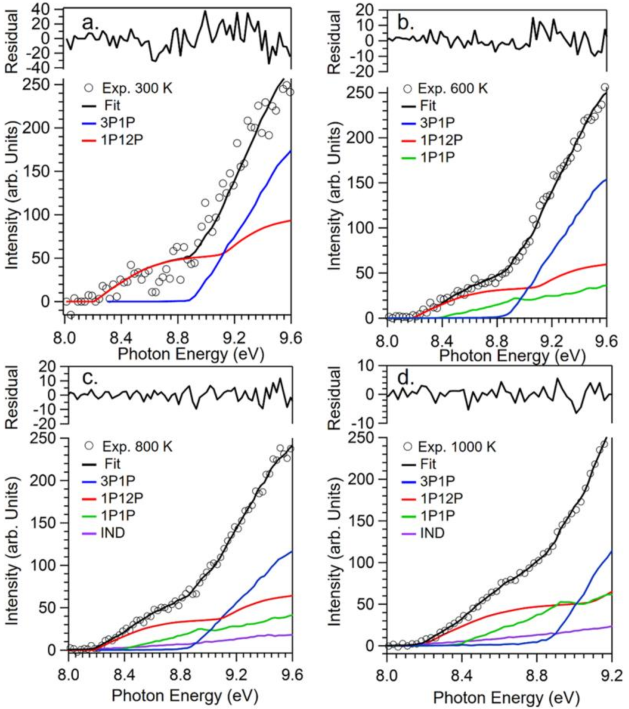
- 3-phenyl-1-propyne = indene
- 3-phenyl-1-propyne = phenyl + propargyl
- 3-phenyl-1-propyne = indenyl + H
- 3-phenyl-1-propyne = C6H5CHCCH + H
  phenylallene = indene
- phenylallene = phenyl + propargyl
- phenylallene =indenyl + H,
- phenylallene = C6H5CHCCH + H
- indene = indenyl + H

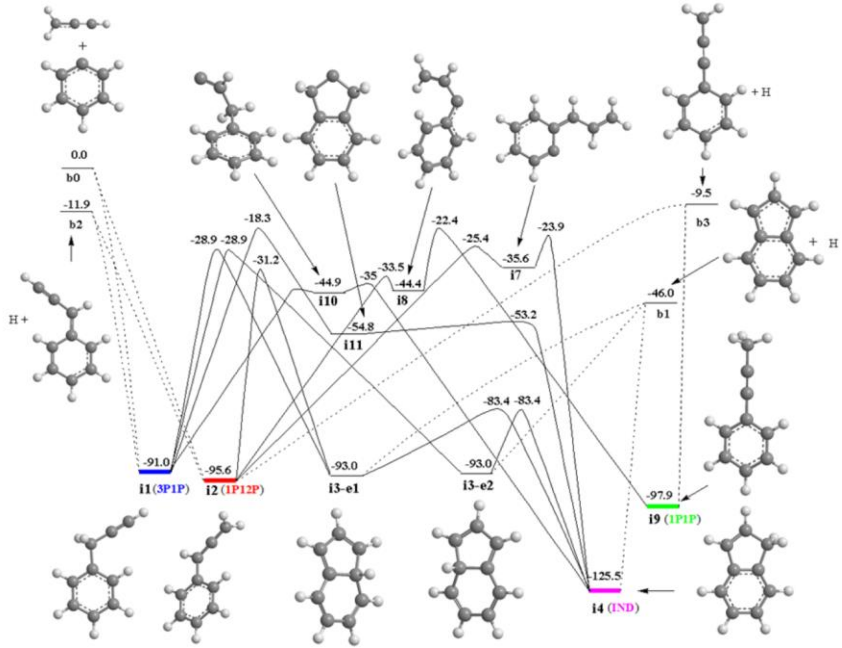


A. N. Morozov and A. M. Mebel, "Theoretical study of the reaction mechanism and kinetics of the phenyl + propargyl association", *Phys. Chem. Chem. Phys.*, **2020,** 22, 6868

$C_6H_5 + C_3H_3$

Kinetics Experiments

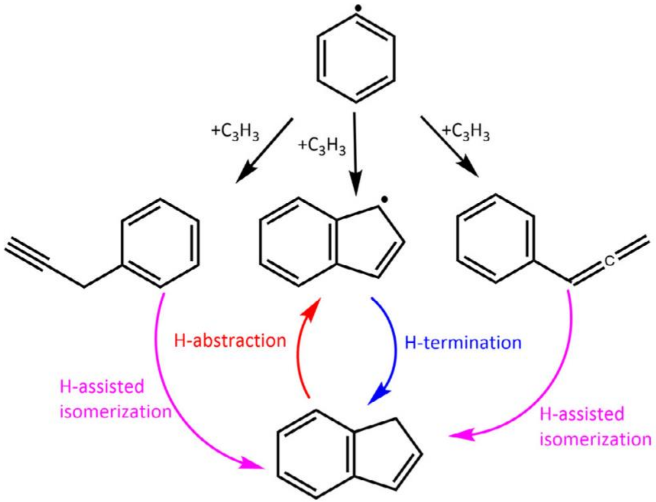


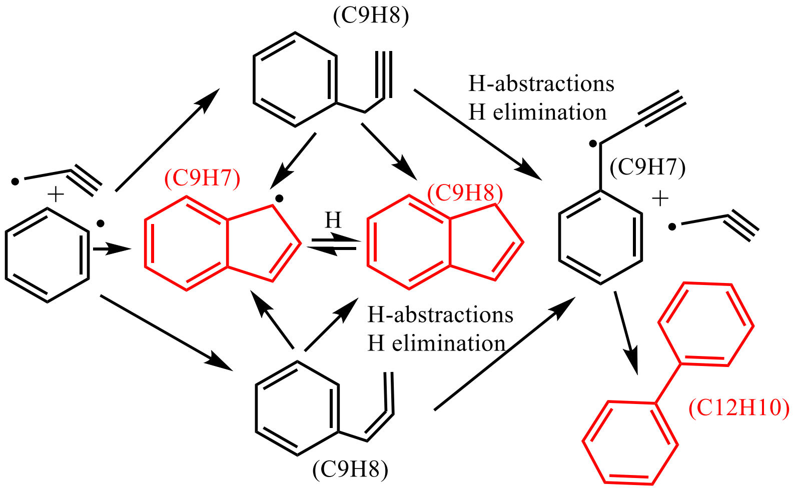


T. M. Selby *et al.,* Radical-Radical Reactions in Molecular Weight Growth: The Phenyl + Propargyl Reaction”, *J. Phys. Chem. A,* **2023,** 127, 2577-2590

$C_6H_5 + C_3H_3$

Flame Experiments: benzene+C3H4 (propyne) and C3H4 (allene and propyne)

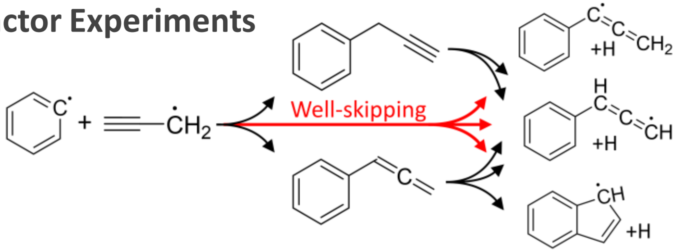


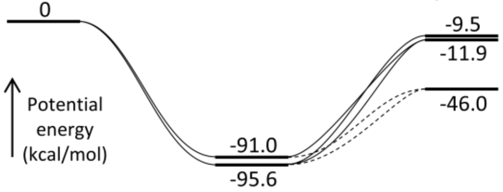


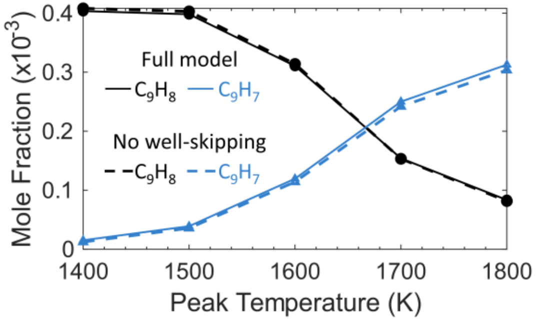
G. Kukkadapu, S. W. Wagnon, W. J. Pitz, N. Hansen, *Proc. Combust. Inst.,* **2021,** 38(1), 1477-1485
N. Hansen, B. Yang, M. Braun-Unkhoff, A. Ramirez, G. Kukkadapu, *Combust. Flame,* **2022,** 243, 112075

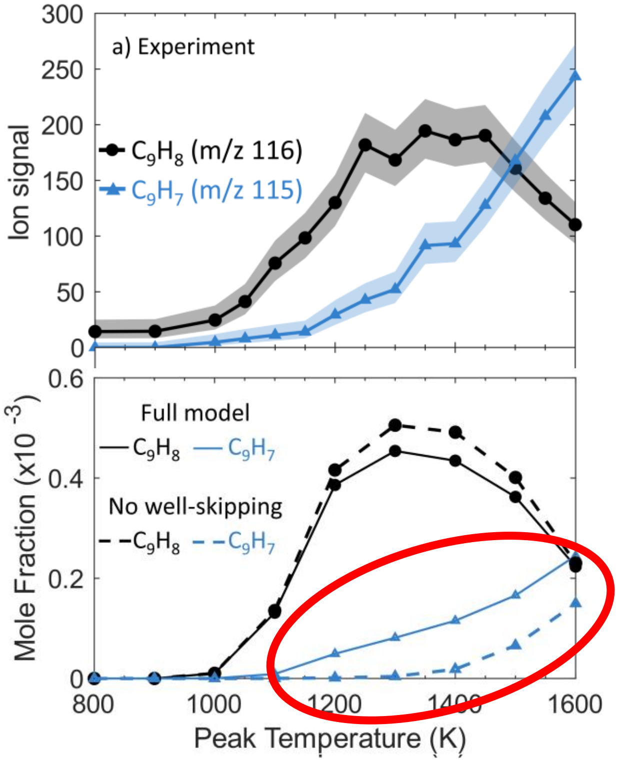
$C_6H_5 + C_3H_3$

Reactor Experiments







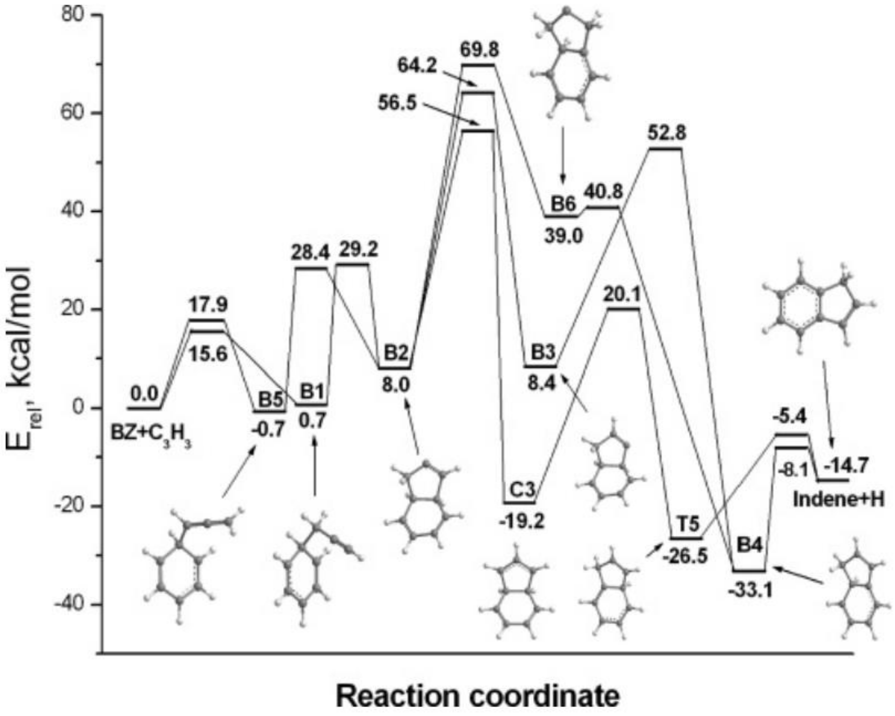


D. E. Couch, G. Kukkadapu, A. J. Zhang, A. W. Jasper, C. A. Taatjes, N. Hansen, *Proc. Combust. Inst.*, **2023**, 39(1), 643-651

$C_6H_6 + C_3H_3$ and $C_6H_5 + C_3H_4$

- the C6H5 + C3H3 recombination mechanism requires less reaction steps to form indene and these steps exhibit lower barriers (within 14-17 kcal/mol), as compared to the pathway starting from C3H3 addition to benzene.

- it costs energy to produce phenyl radical from benzene and the contribution of each pathway will depend on combustion conditions, such as temperature, pressure, fuel type, radical concentrations, etc., and can be clarified in kinetic simulations of particular combustion systems.



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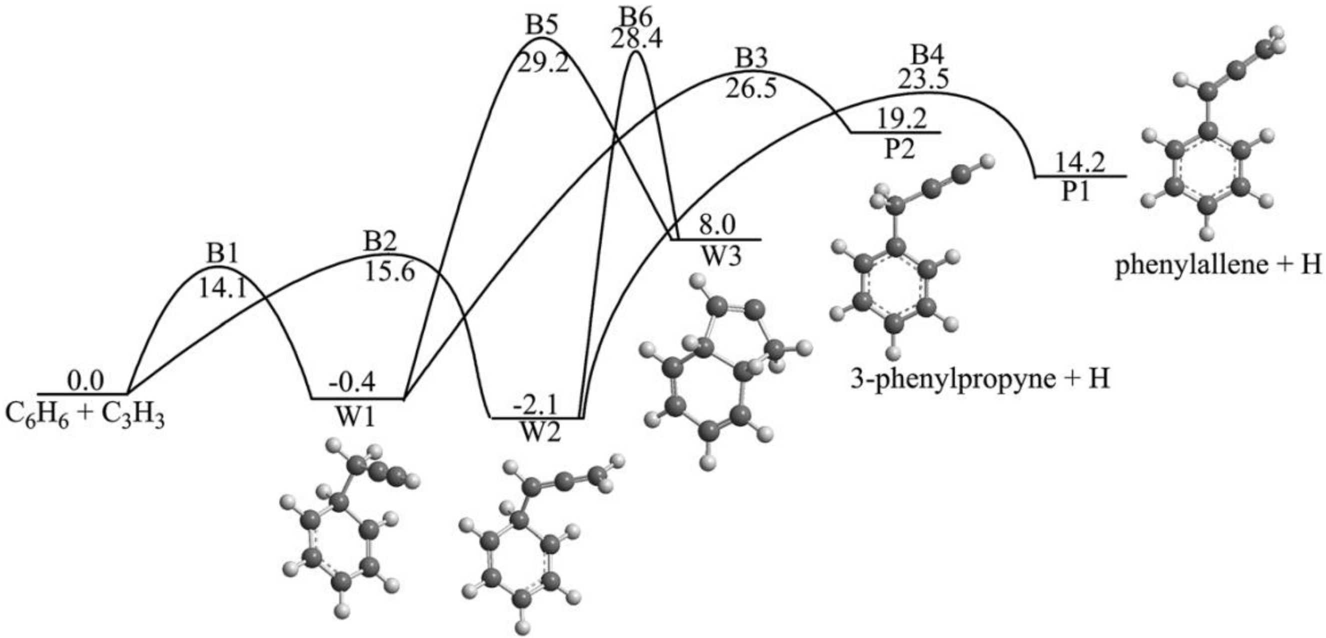
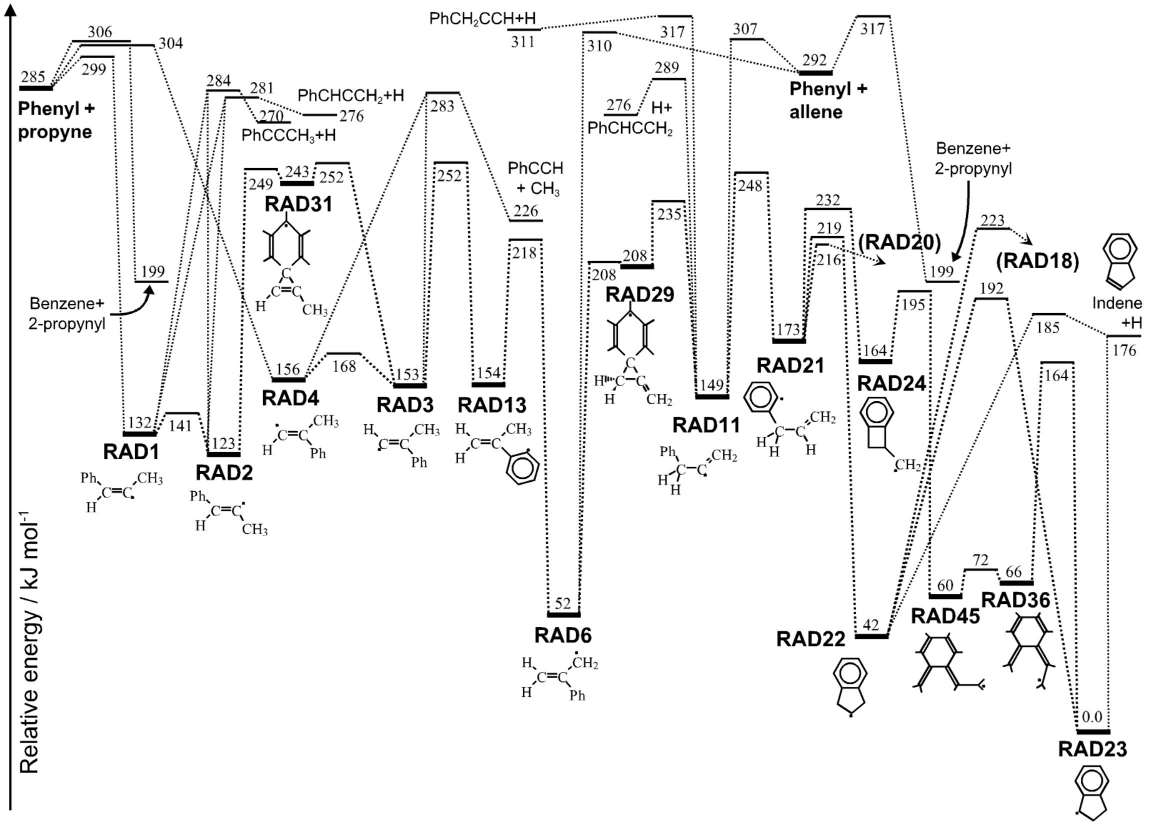
$C_6H_6 + C_3H_3$ and $C_6H_5 + C_3H_4$



A. M. Mebel *et al.*, “Pressure-dependent rate constants for PAH growth: formation of indene and its conversion to naphthalene”, *Faraday Discuss.*, **2016,** 195, 637-670

$C_6H_5 + C_3H_4$

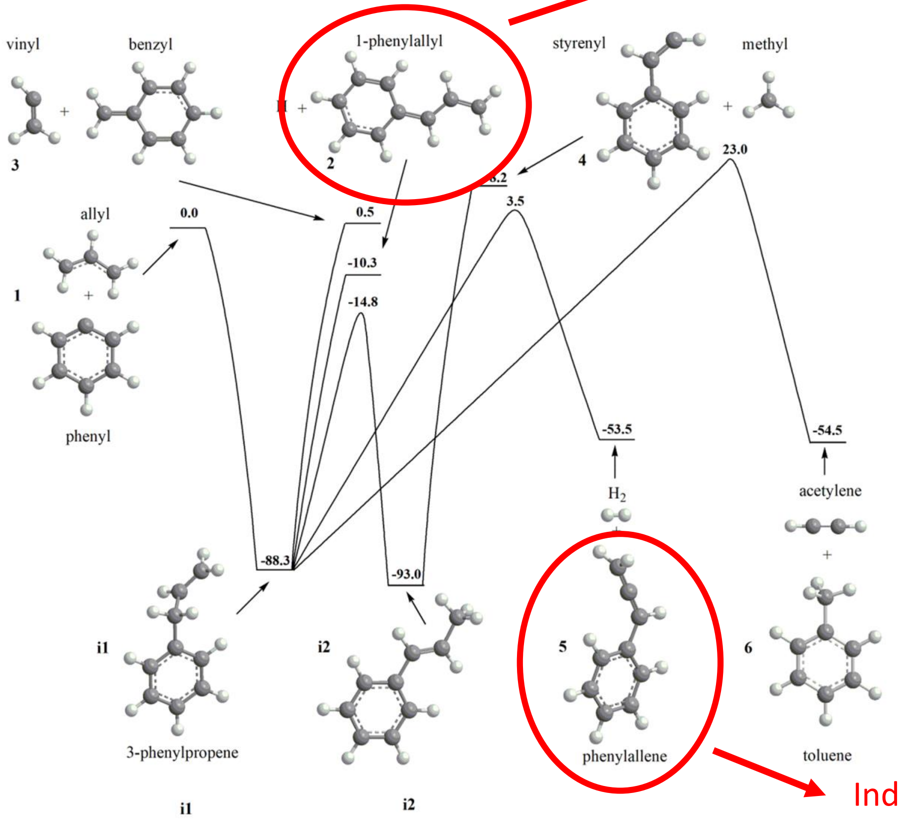
- the reactions of C3HX species can be important sinks for phenyl, with a summed contribution rivaling the important C2H2 reaction path
- the product distribution of the phenyl + C3H4 reactions are complex, leading to a plethora of substituted acetylenes and allenes, as well as indene, benzyl, and a number of stabilized C9H9 radicals, depending on temperature and pressure



L. Vereecken *et al.*, "Reaction of Phenyl Radicals with Propyne", *J. Am. Chem. Soc.*, **2002,** 124(11), 2781-2789

L. Vereecken and J. Peeters, "Reactions of chemically activated C9H9 species II: The reaction of phenyl radicals with allen and cyclopropane, andof benzyl radicals with acetylene", *Phys. Chem. Chem. Phys.*, **2003,** 5, 2807-2817

$C_6H_5 + C_3H_5$

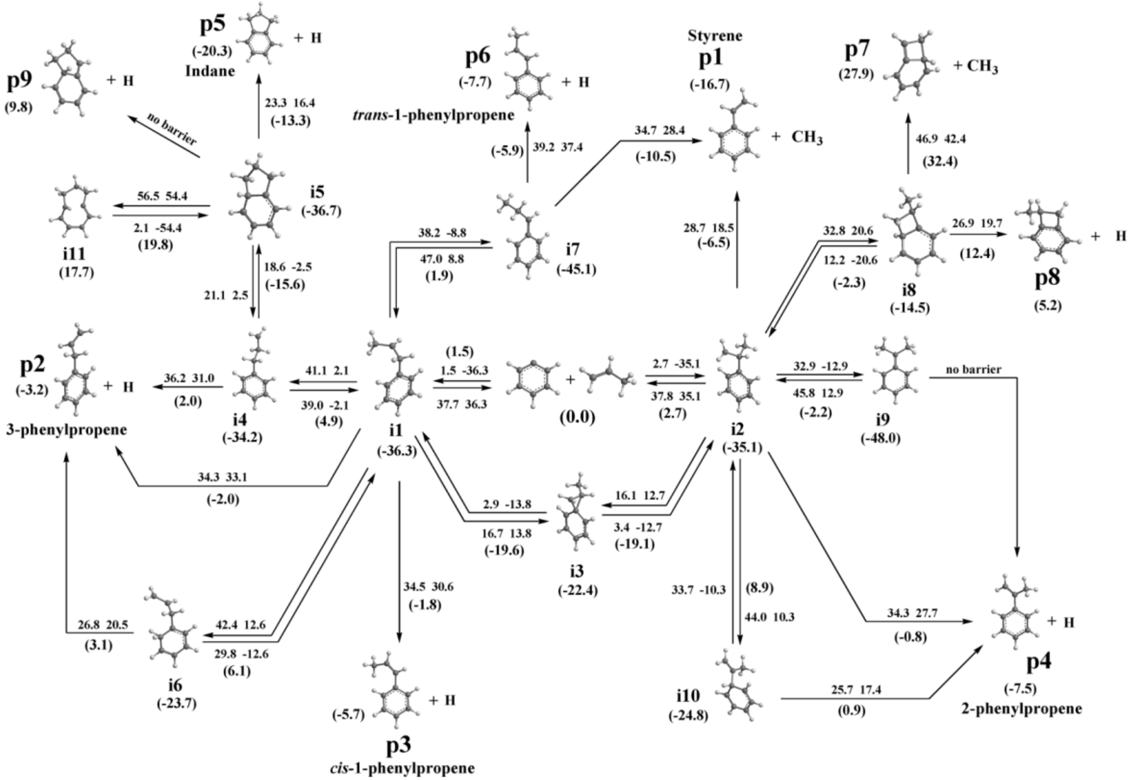


Indene + H

Indene

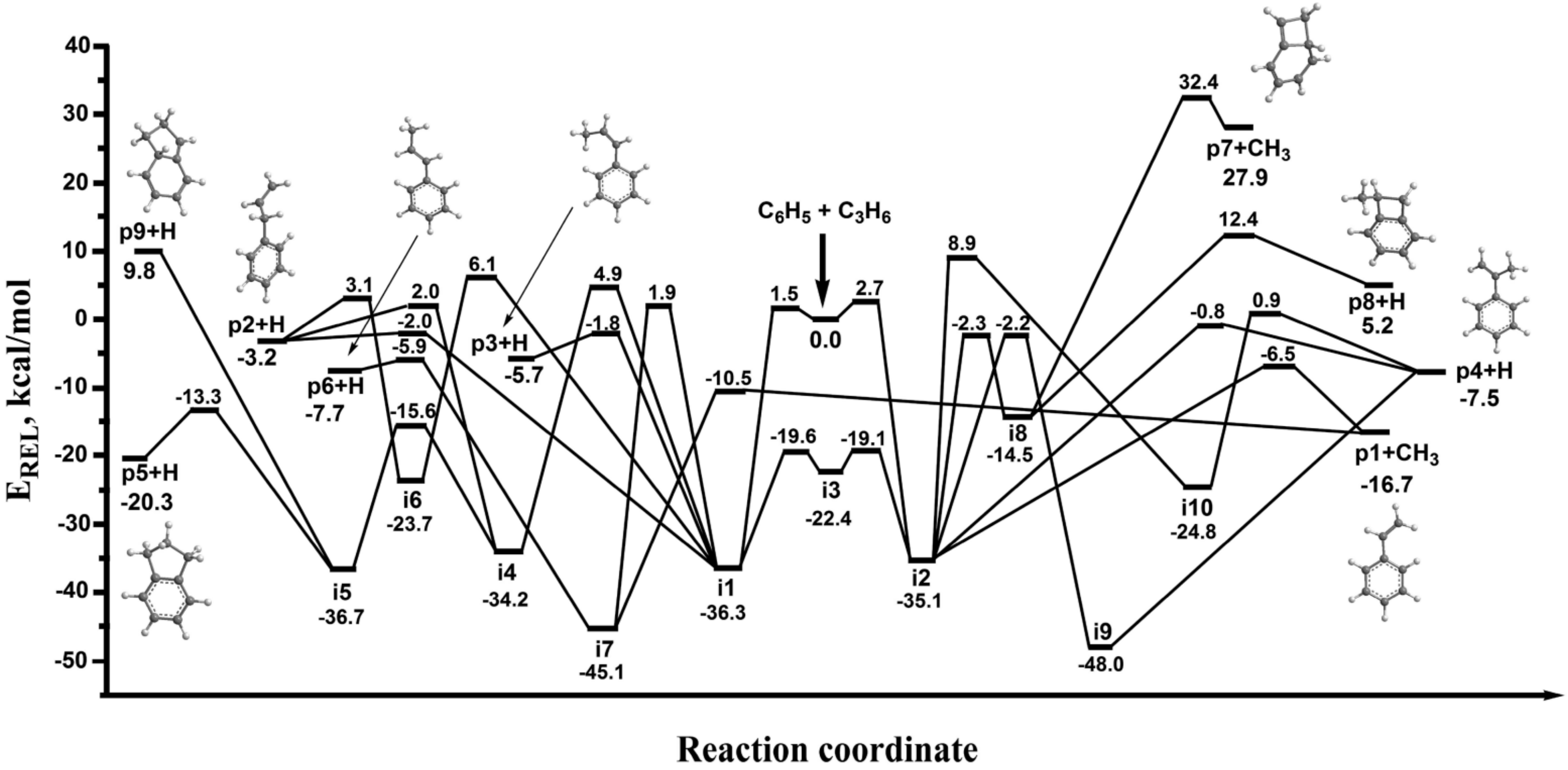
A. N. Morozov and A. M. Mebel, “Theoretical Study of the Reaction Mechanism and Kinetics of the Phenyl + Allyl and Related Benzyl + Vinyl Associations”, *J. Phys. Chem. A*, **2019,** 123, 1720-1729

$C_6H_5 + C_3H_6$



V. V. Kislov *et al.,* "Reaction of Phenyl Radical with propylene as a Possible Source of Indene and Other Polycyclic Aromatic Hydrocarbons: An Ab Initio/RRKM-ME Study", *J. Phys. Chem. A,* **2012,** 116, 4176-4191

$C_6H_5 + C_3H_6$



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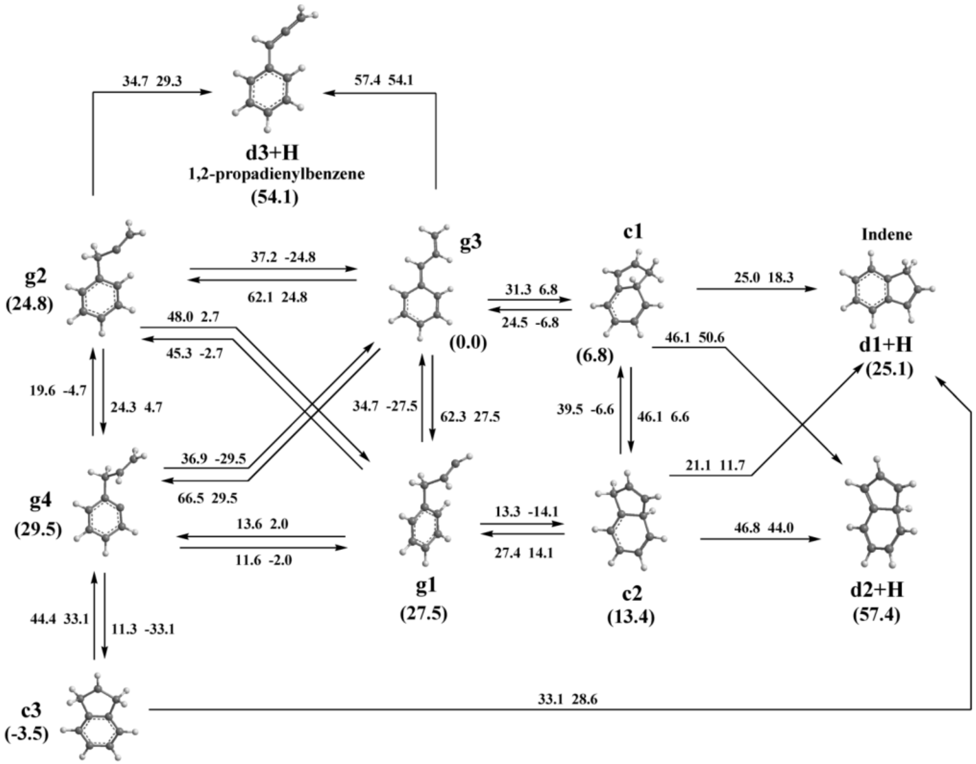
$C_6H_5 + C_3H_6$



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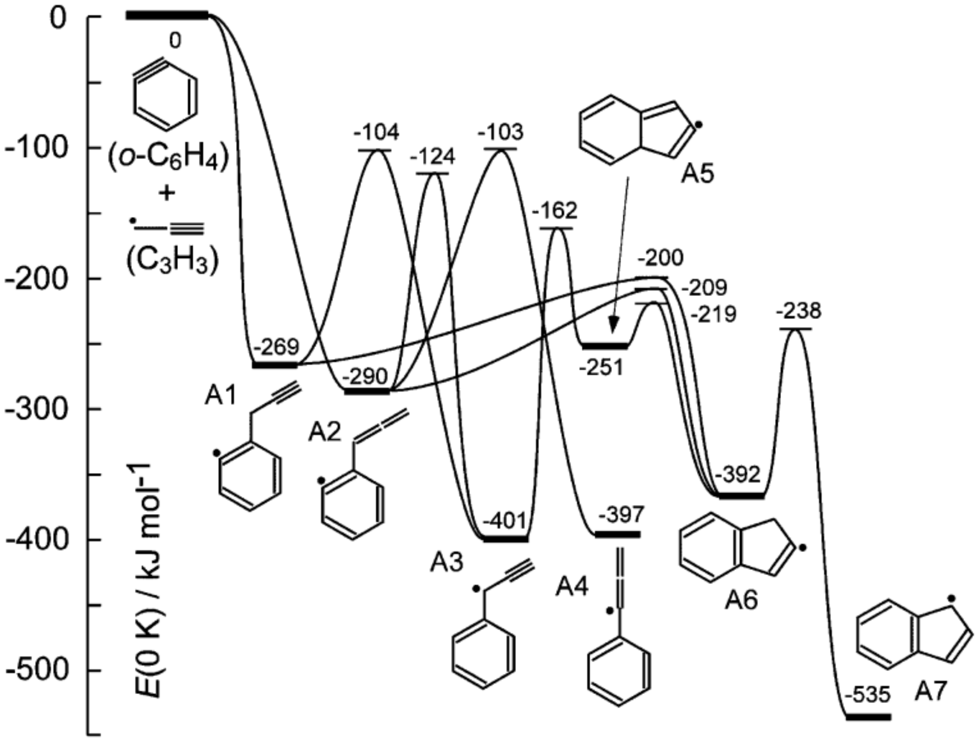
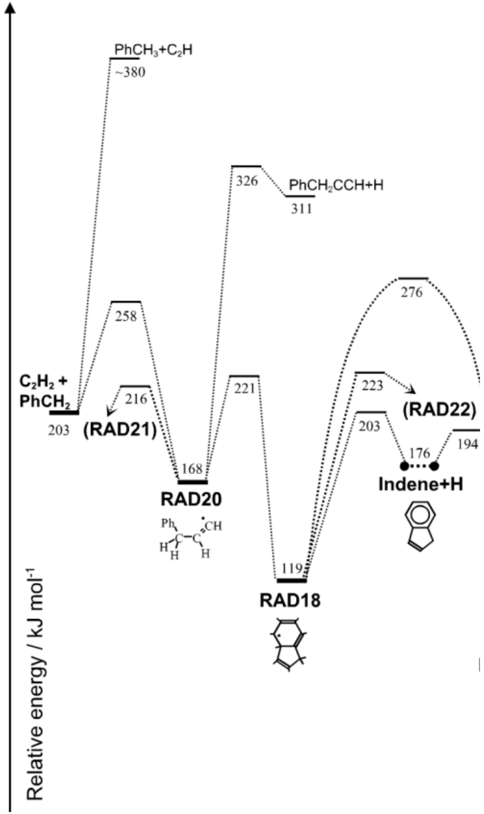
$C_6H_4 + C_3H_3$



A. Matsugi and A. Miyoshi, “Reactions of o-benzyne with propargyl and benzyl radicals: potential sources of polycyclic aromatic hydrocarbons in combustion”, *Phys. Chem. Chem. Phys.*, **2012,** 14, 9722-9728

$C_7H_7 + C_2H_2$

- introduced by Bittner and Howard (*Proc. Combust. Inst.,* **1981,** 18, 1105-1116(
- hydrogen abstraction is negligible in the reaction of PhCH2 radicals with C2H2 , as the formation of toluene + ethynyl is highly endothermic due to the loss of the radical electron resonance stabilization, and the exchange of a strong acetylenic C–H-bond against a regular primary C–H bond
- Despite extensive electron delocalization in benzyl, addition will occur only with –CH2 radical site, as the electron density on the –CH2 group is about 3 times higher than on the phenyl carbons, and as the other possible sites break the phenyl substituent π-aromaticity.
- The initial adduct (Rad20) can undergo a ring-closure and an H-elimination to form indene + H



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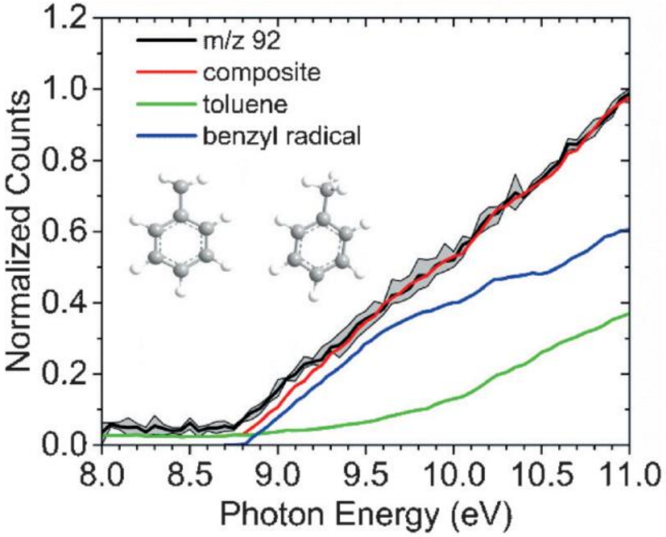
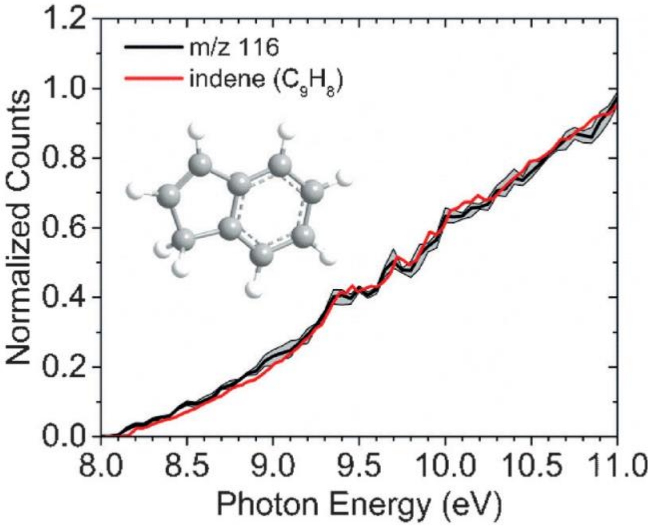
$C_7H_7 + C_2H_2$

High-Temperature Reactor Experiments:

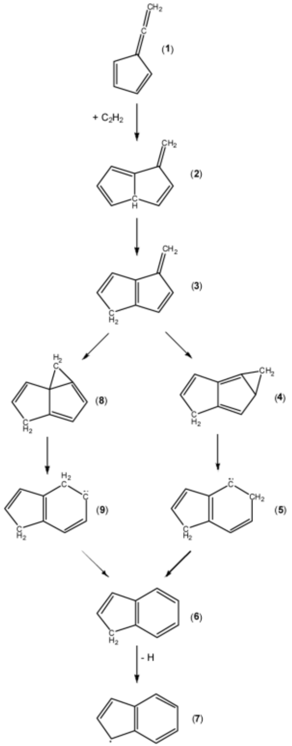
the facile formation of indene (C9H8) through the bimolecular reaction of the benzyl radical (C7H7) with acetylene (C2H2) provides compelling evidence of the formation of the simplest PAH, carrying a six- and a five-membered ring, under combustion-like conditions.

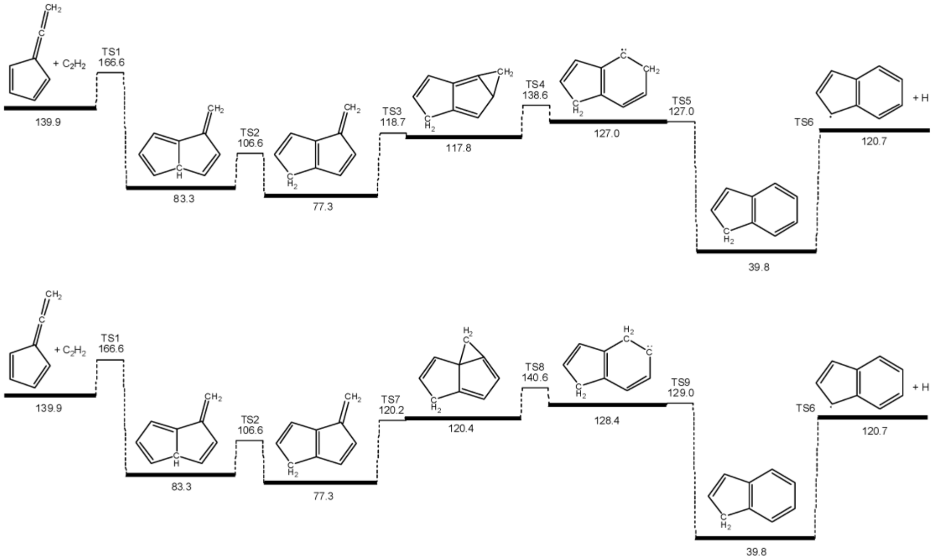




D. S. N. Parker *et al.,* “Selective Formation of Indene through the Reaction of Benzyl Radicals with Acetylene”, *ChemPhysChem,* **2015,** 16, 2091-2093

$C_7H_5 + C_2H_2$

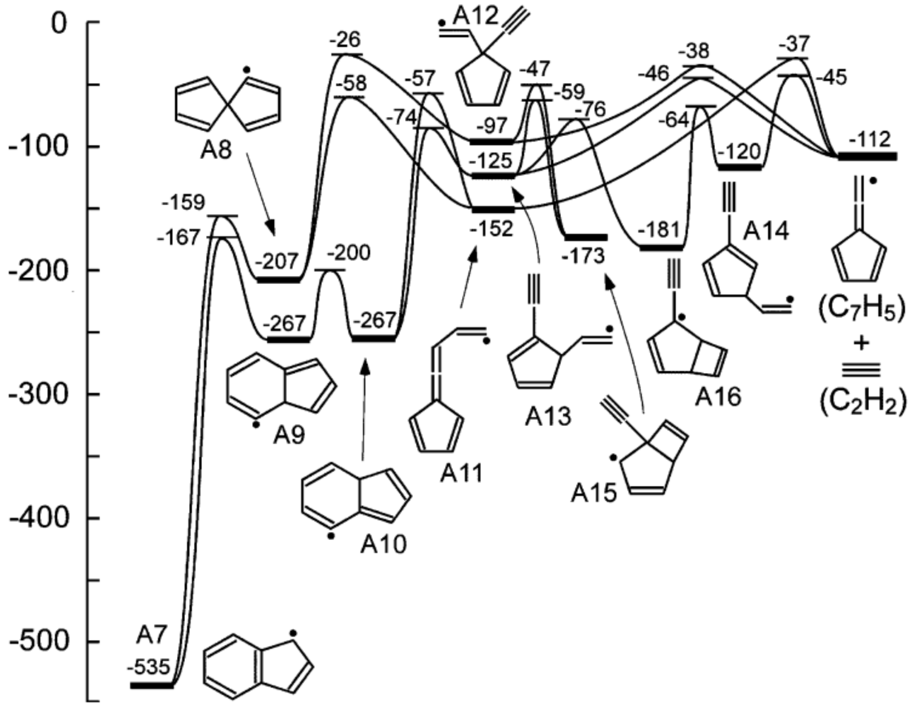




- ➢ As the fulvenallene + C2H2 reaction proceeds at a rate approaching that of the benzyl + C2H2 reaction at combustion temperatures
- ➢ the importance of this new mechanism will depend largely on the relative concentrations of benzyl and fulvenallene

G. Da Silva and J. W. Bozzelli, “Indene Formation from Alkylated Aromatics: Kinetics and Products of the Fulvenallene + Acetylene Reaction”, *J. Phys. Chem. A,* **2009,** 113, 8971-8978

$C_7H_5 + C_2H_2$



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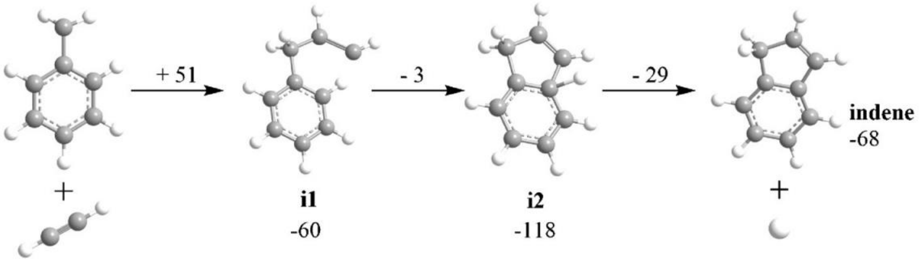
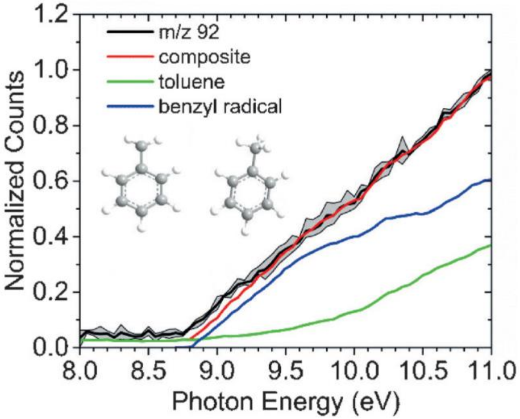
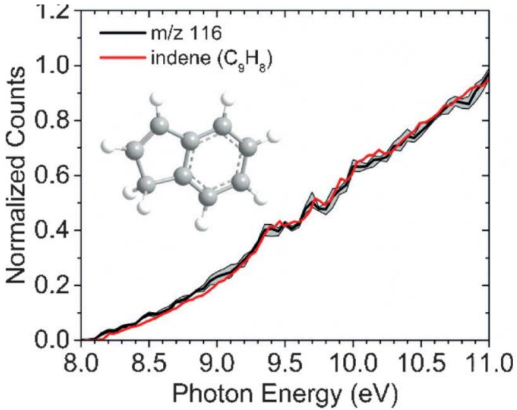
$C_7H_5 + C_2H_2$

High-Temperature Reactor Experiments:







D. S. N. Parker *et al.*, “Selective Formation of Indene through the Reaction of Benzyl Radicals with Acetylene”, *ChemPhysChem*, **2015,** 16, 2091-2093

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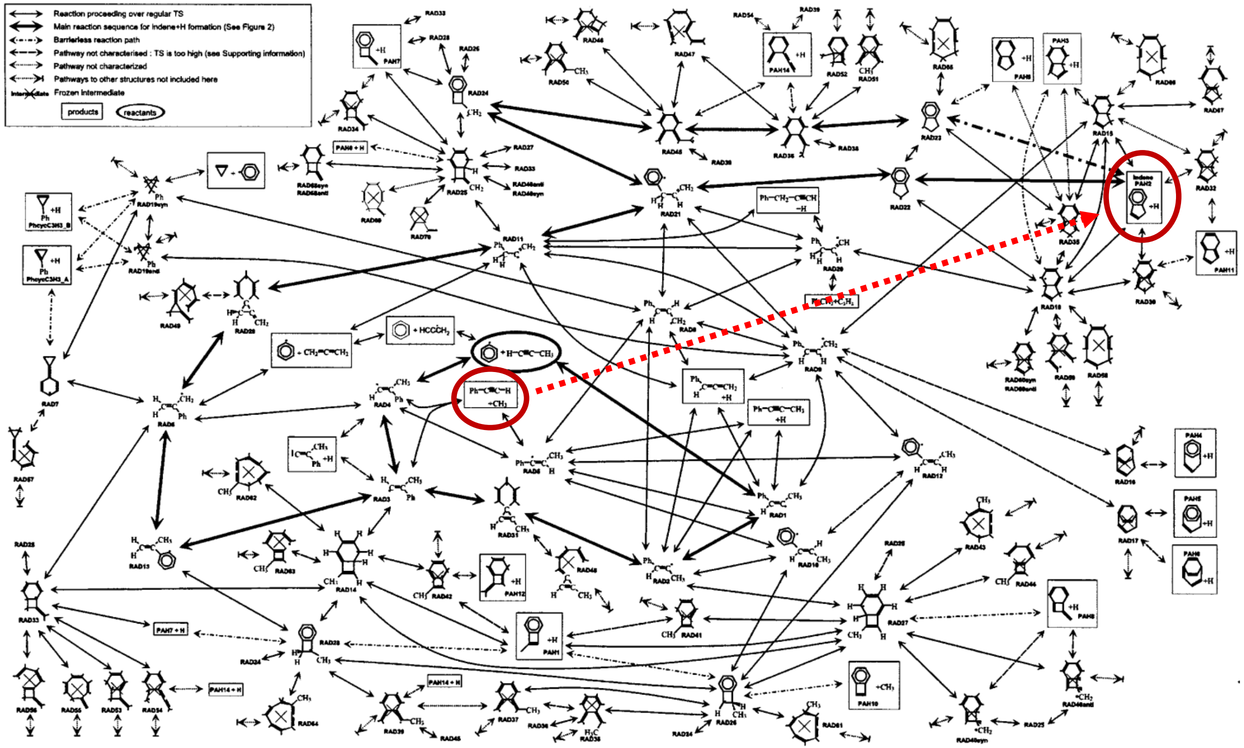
$C_8H_6 + CH_3$



L. Vereecken *et al.*, “Reaction of Phenyl Radicals with Propyne”, *J. Am. Chem. Soc.*, **2002,** 124(11), 2781-2789
A. M. Mebel et al., “Pressure-dependent rate constants for PAH growth: formation of indene and its conversion to naphthalene”, *Faraday Discuss.*, **2016,** 195, 637

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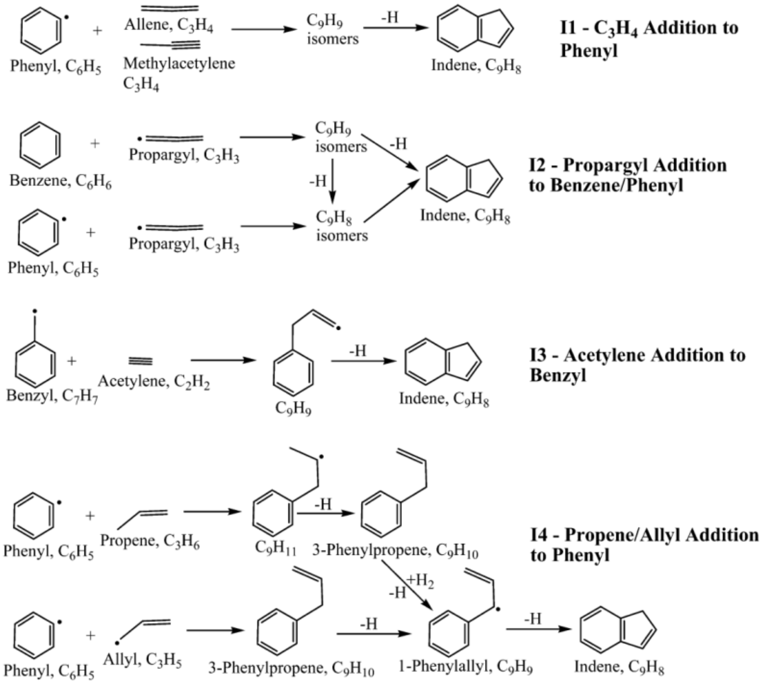
Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

Lecture 6: Ring-Enlargements and Other Pathways

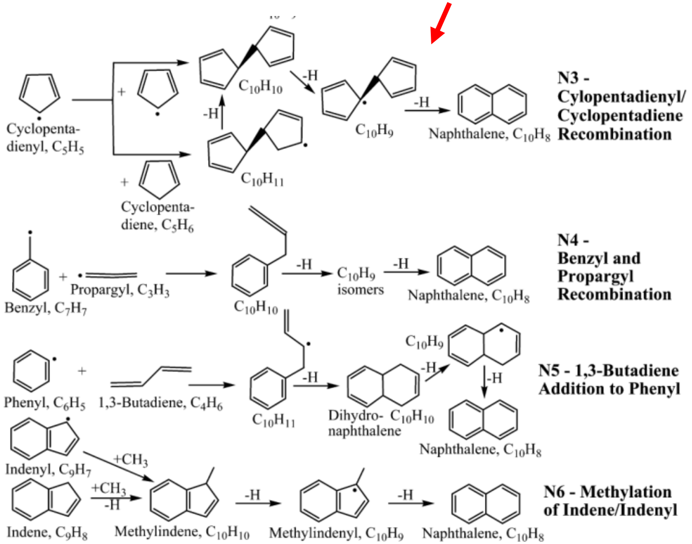
Nils Hansen

Sandia National Laboratories

Five-Membered Ring Species



Ring-Enlargements



Ring-Enlargements

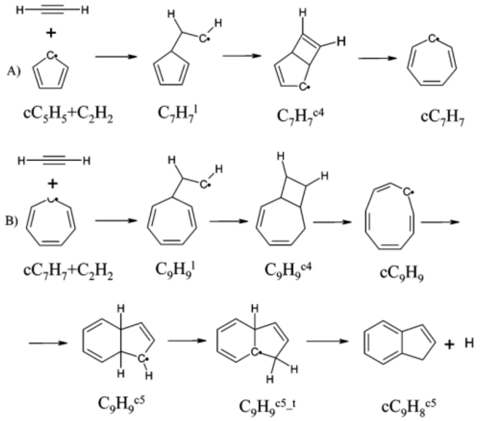
A. M. Mebel, A. Landera, and R. I. Kaiser, “Formation Mechanisms of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames”, J. *Phys. Chem. A,* **2017,** 121, 901-926

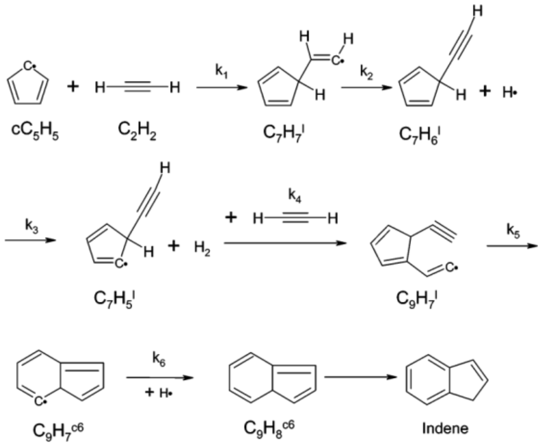
Ring-Enlargement Reactions

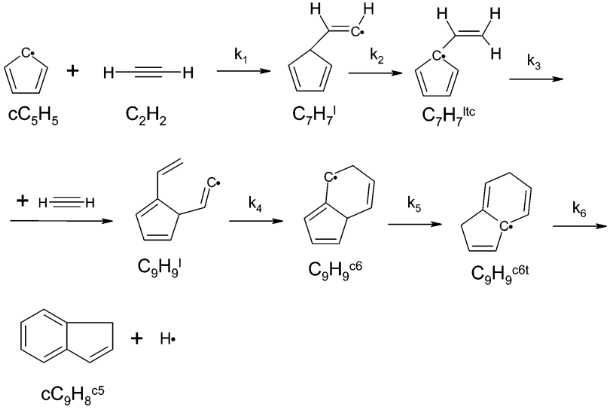
We already talked about **fulvene to benzene, indene + methyl = naphthalene, and 2 x cyclopentadienyl = naphthalene**

Other reactions may include:

$C_5H_5 + CH_3 = C_6H_6 + 2H$
$C_5H_5 + C_2H_2 = C_7H_7$
$C_5H_5 + C_3H_3 = C_8H_8$



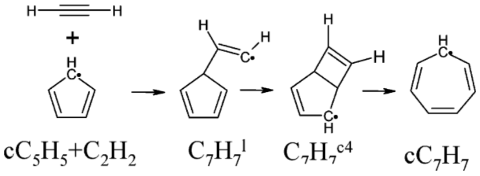




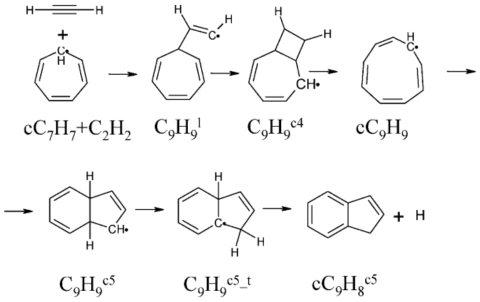
A. S. Fascella, C. Cavallotti, R. Rota, and S. Carra, “The Peculiar Kinetics of the Reaction between Acetylene and the Cyclopentadienyl Radical”, J. *Phys. Chem. A,* **2005,** 109, 7546-7557

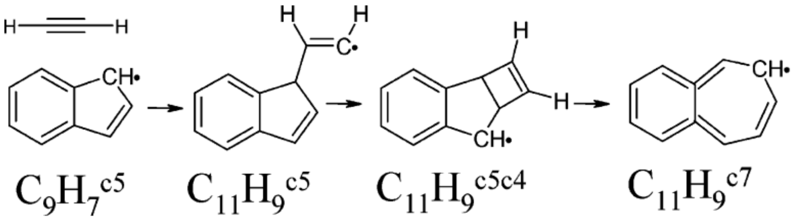
Ring-Enlargement Reactions

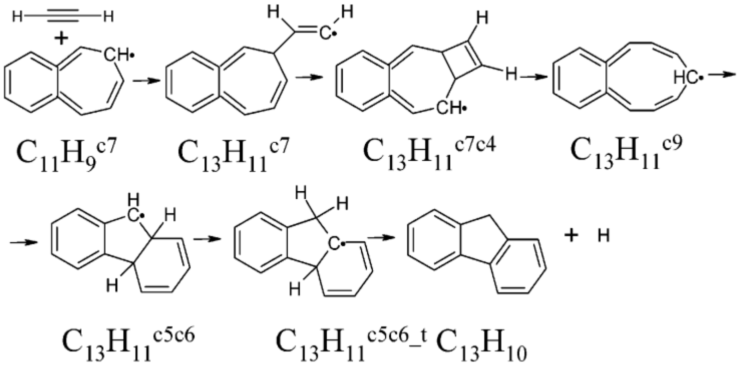
SCHEME 1: Kinetic Pathway Proposed To Describe the Reactivity Originated by the Addition of Acetylene to cC_5H_5 in Which the Cycloheptatrienyl Radical Appears as the Product



SCHEME 2: Kinetic Mechanism Proposed To Describe the Reactivity Originated by the Addition of Acetylene to cC_7H_7



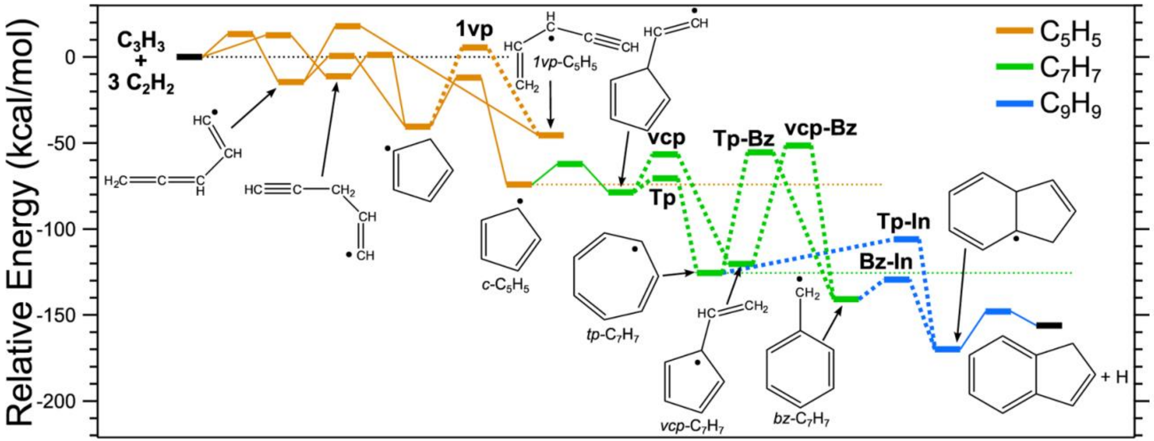


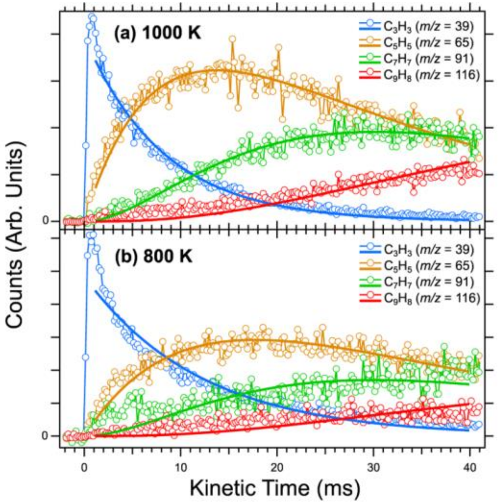


C. Cavallotti, S. Mancarella, R. Rota, and S. Carra, “Conversion of C5 into C6 Cyclic Species through the Formation of C7 Intermediates”, *J. Phys. Chem. A,* **2007,** 111, 3959-3969

Ring-Enlargement Reactions – $C_5H_5 + C_2H_2$

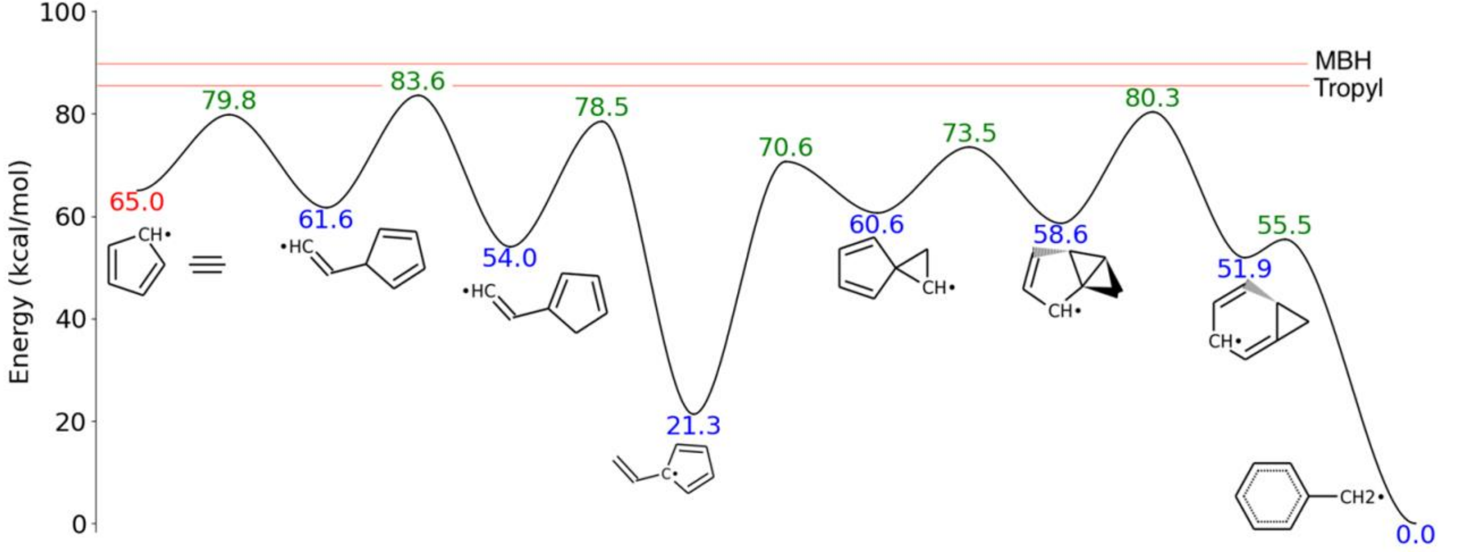
Kinetic Experiments:





J. D. Savee *et al.*, "Time- and Isomer-Resolved Measurements of Sequential Addition of Acetylene to the Propargyl Radical", *J. Phys. Chem. Lett.*, **2015**, 6, 4153-4158

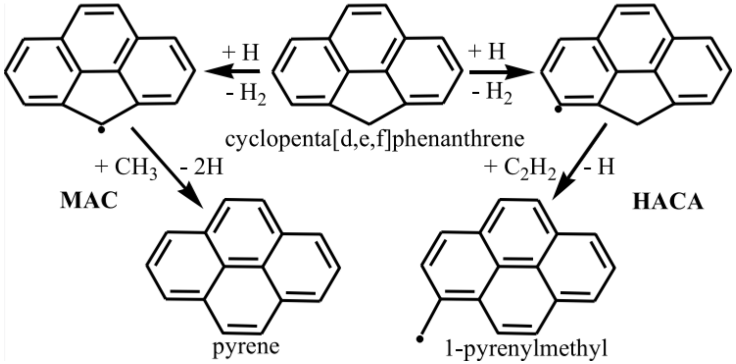
Ring-Enlargement Reactions – $C_5H_5 + C_2H_2$

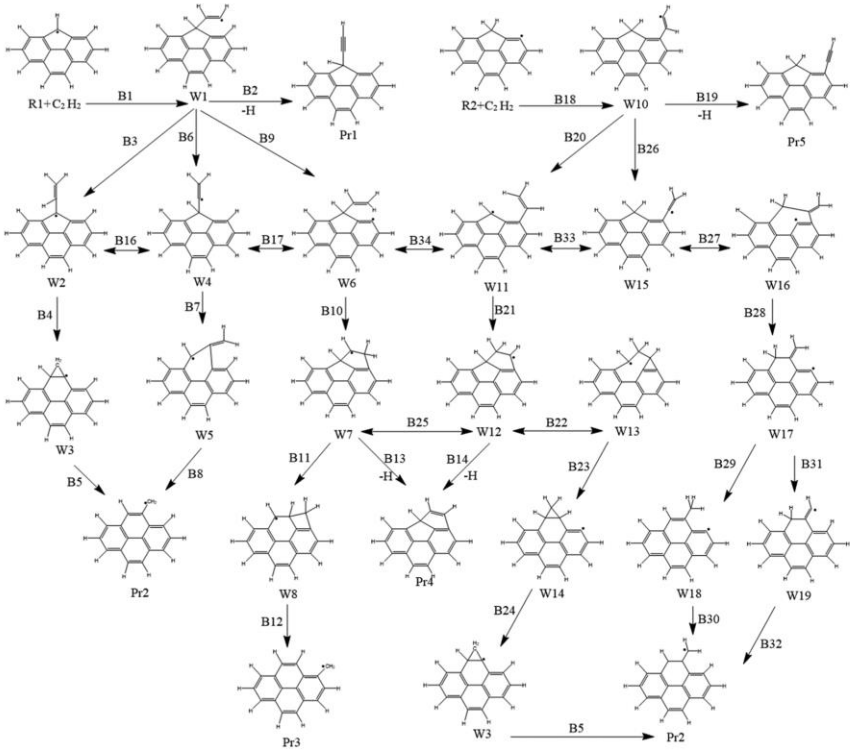


C. Marti, H. A. Michelsen, H. N. Najm, J. Zador, “Comprehensive Kinetics on the C7H7 Potential Energy Surface under Combustion Conditions”, *J. Phys. Chem. A,* **2023,** 127, 1941-1959

GAS PHASE CHEMICAL PHYSICS

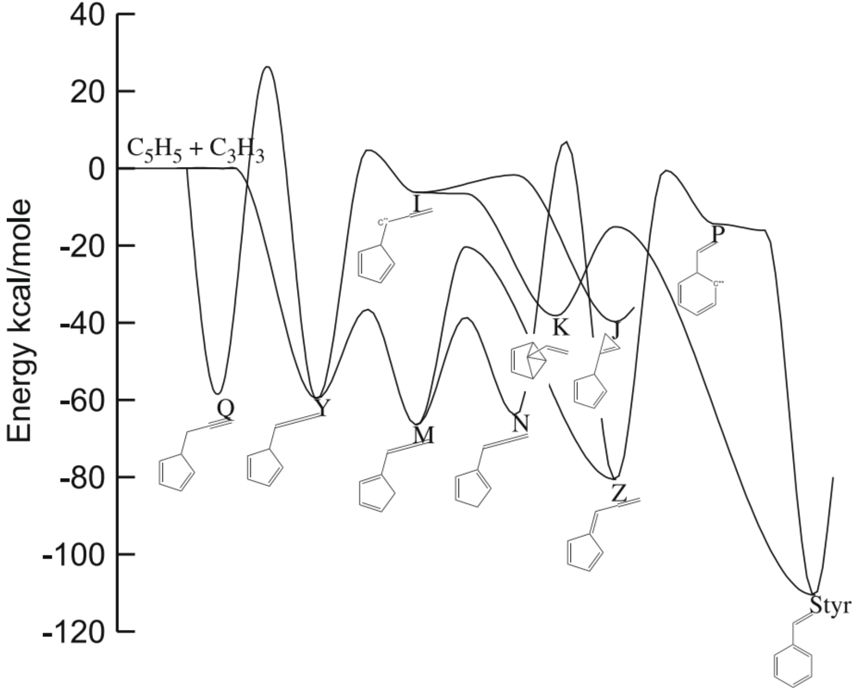
Ring-Enlargement Reactions

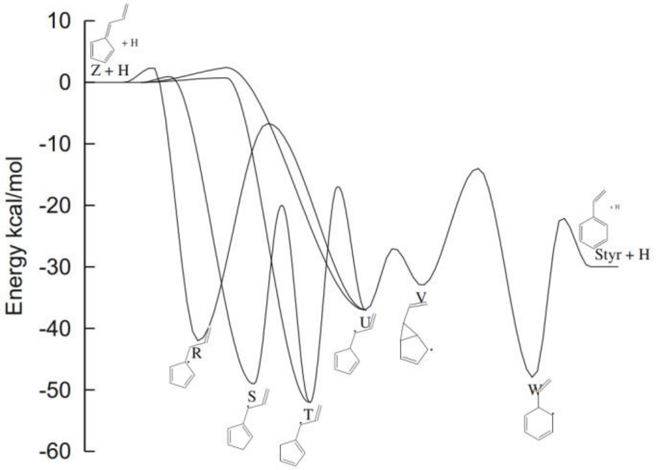




A. S. Semenikhin *et al.*, “Transformation of an Embedded Five-Membered Ring in Polycyclic Aromatic Hydrocarbons via the Hydrogen-Abstraction-Acetylene-Addition Mechanism: A Theoretical Study”, *J. Phys. Chem. A,* **2021,** 125, 3341-3354

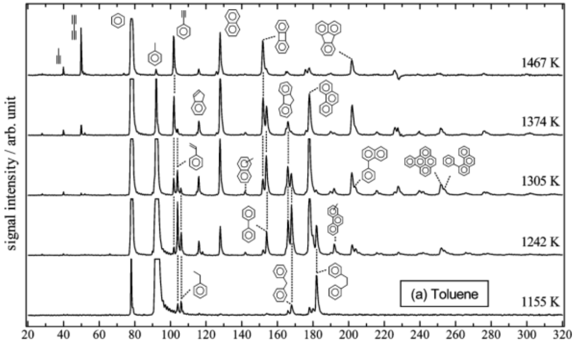
Ring-Enlargement Reactions – $C_5H_5 + C_3H_3$

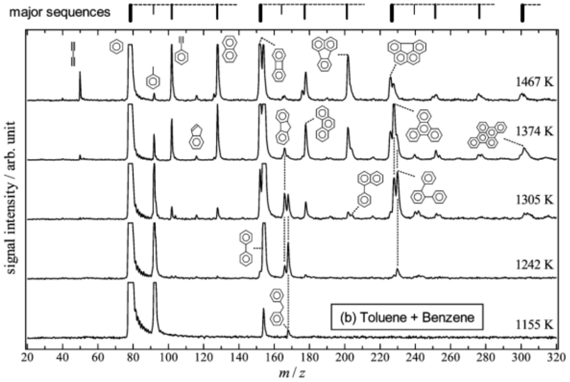


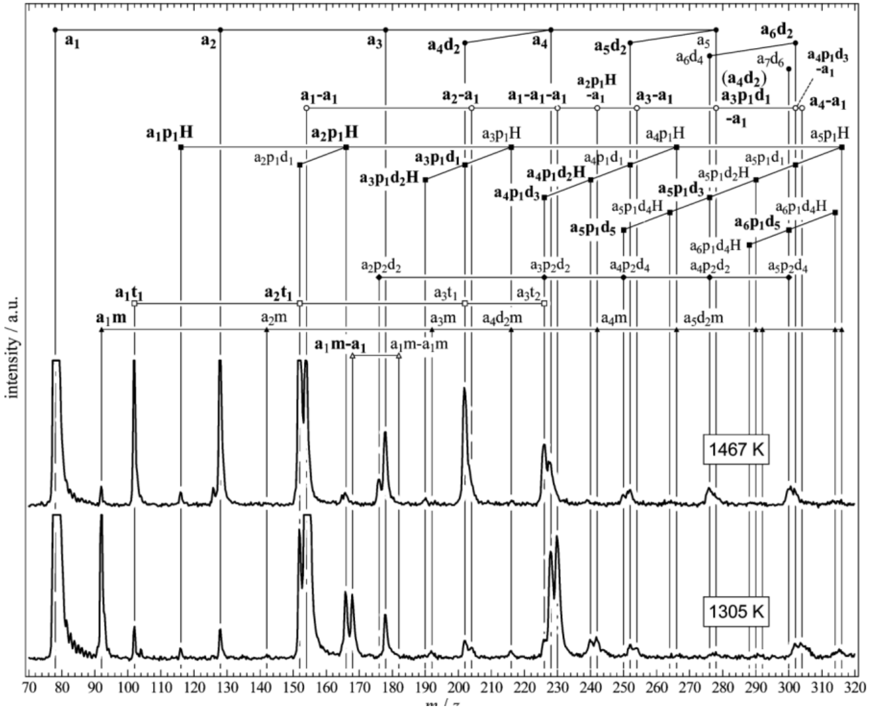


S. Sharma, M. R. Harper, W. H. Green, "Modeling of 1,3-hexadiene, 2,4-hexadiene and 1,4-hexadiene-doped methane flames: Flame modeling, benzene and styrene formation", *Combust. Flame,* **2010,** 157, 1331-1345

The role of phenyl radicals



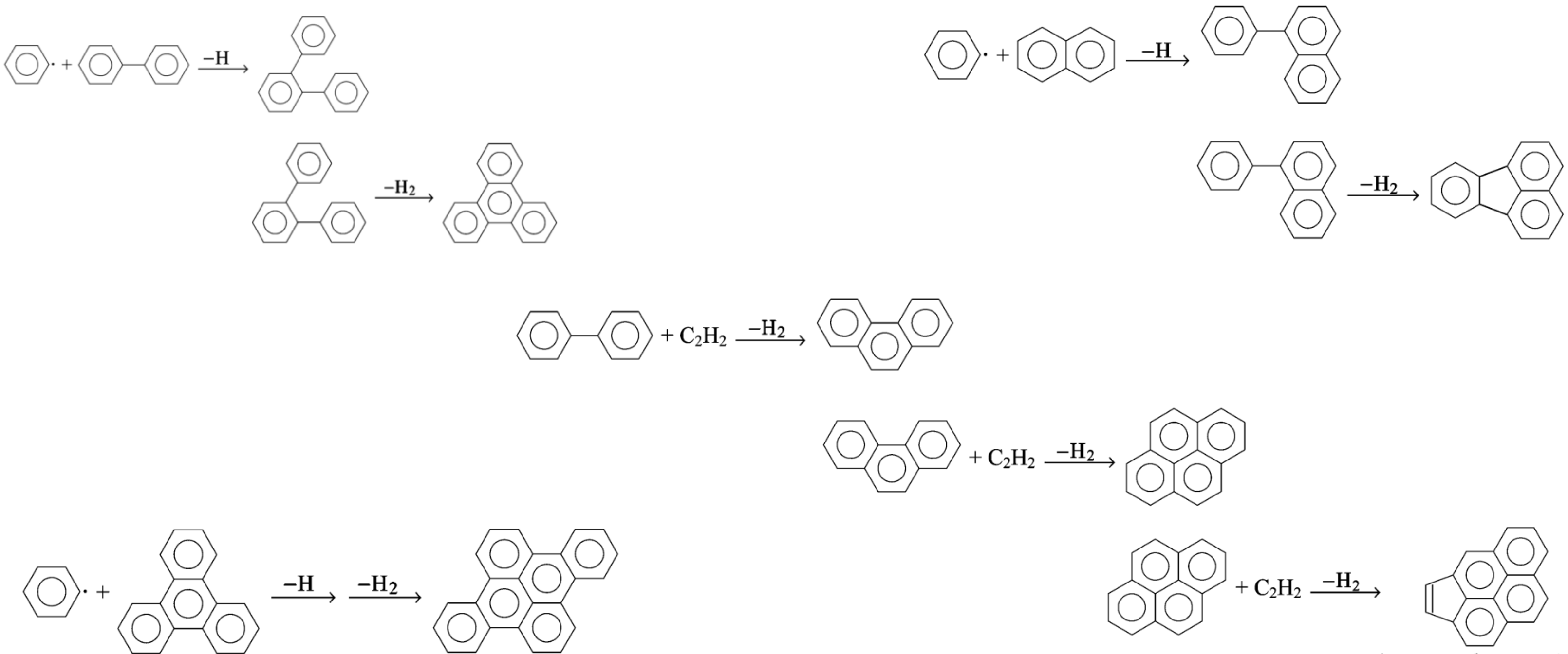




B. Shukla, A. Susa, A. Miyoshi, and M. Koshi, “Role of Phenyl Radicals in the Growth of Polycyclic Aromatic Hydrocarbons”, *J. Phys. Chem. A,* **2008,** 112, 2362-2369

GAS PHASE CHEMICAL PHYSICS

The role of phenyl radicals

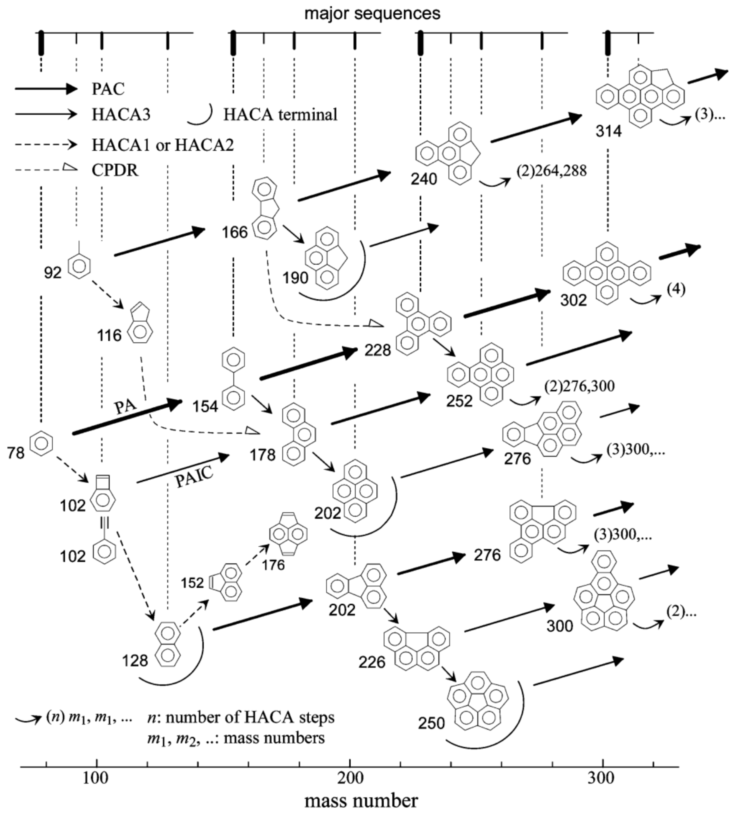


cyclopenta[*cd*]pyrene (**$a_4p_1d_3$**)

B. Shukla, A. Susa, A. Miyoshi, and M. Koshi, “Role of Phenyl Radicals in the Growth of Polycyclic Aromatic Hydrocarbons”, *J. Phys. Chem. A,* **2008,** 112, 2362-2369

GAS PHASE CHEMICAL PHYSICS

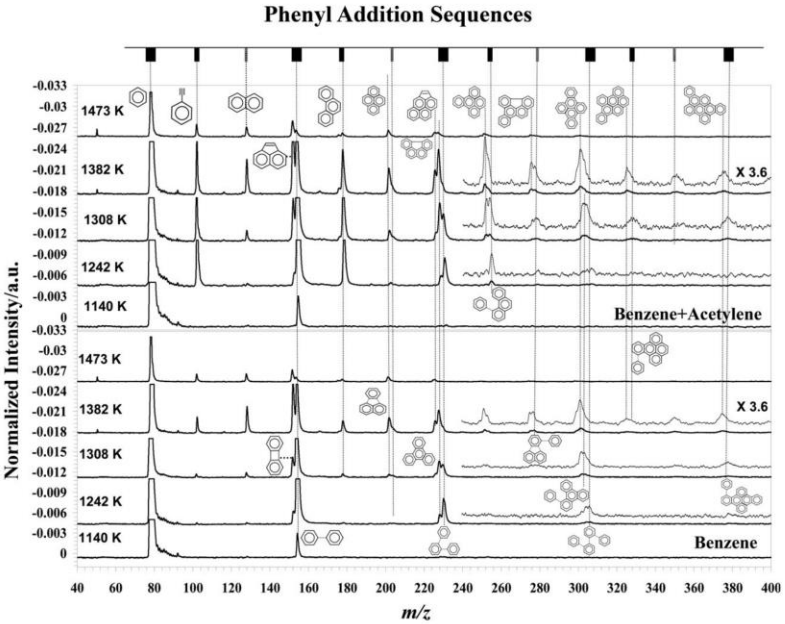
The role of phenyl radicals

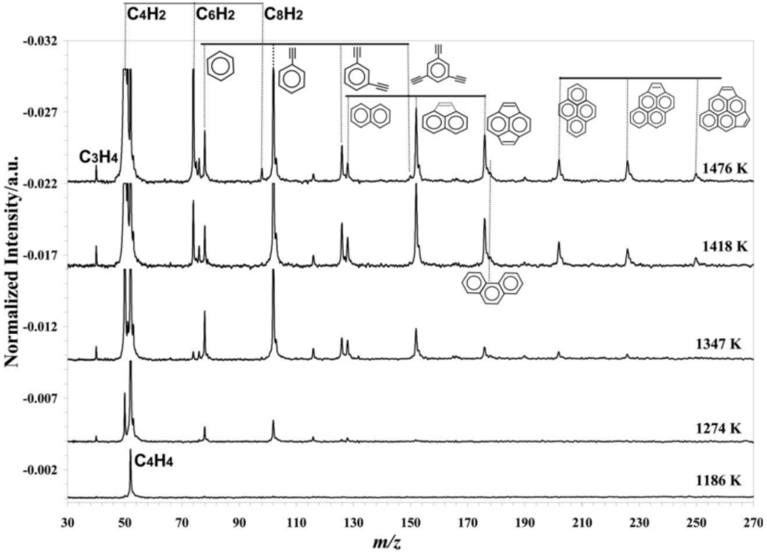


PAC (phenyl addition cyclization) is efficient for PAHs and produces and grows PAHs with five-membered rings.

B. Shukla, A. Susa, A. Miyoshi, and M. Koshi, “Role of Phenyl Radicals in the Growth of Polycyclic Aromatic Hydrocarbons”, *J. Phys. Chem. A*, **2008,** 112, 2362-2369

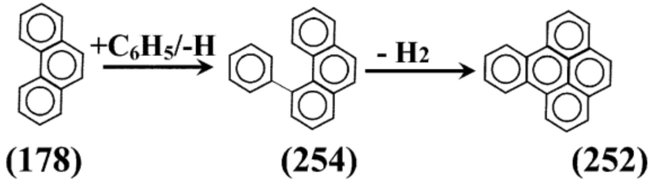
The role of phenyl radicals

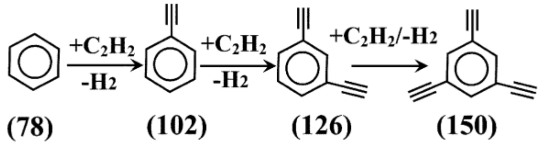


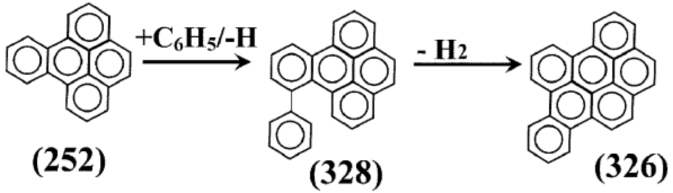


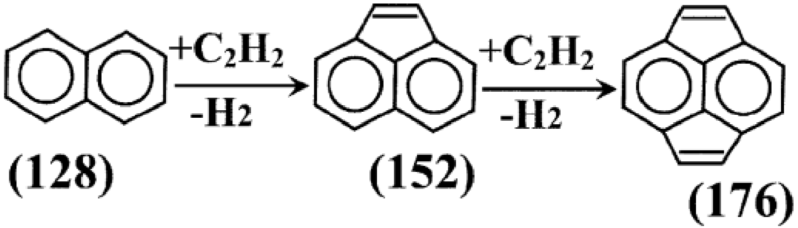
B. Shukla and M. Koshi, “A highly efficient growth mechanism of polycyclic aromatic hydrocarbons”, *Phys. Chem. Chem. Phys.*, **2010,** 12, 2427-2437

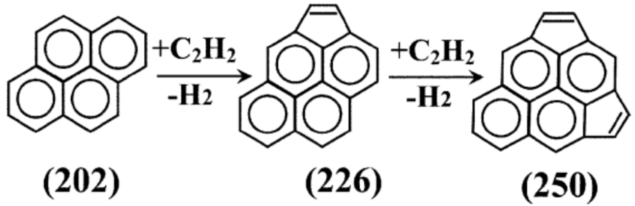
The role of phenyl radicals





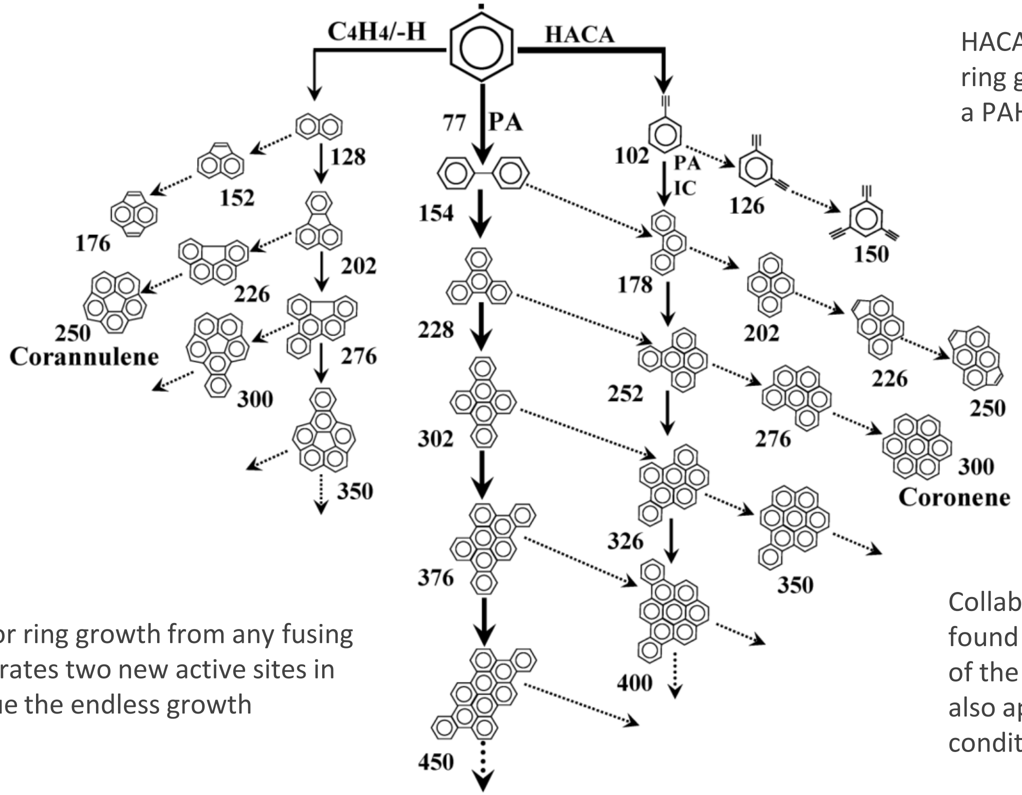






B. Shukla and M. Koshi, "A highly efficient growth mechanism of polycyclic aromatic hydrocarbons", *Phys. Chem. Chem. Phys.*, **2010,** 12, 2427-2437

The role of phenyl radicals



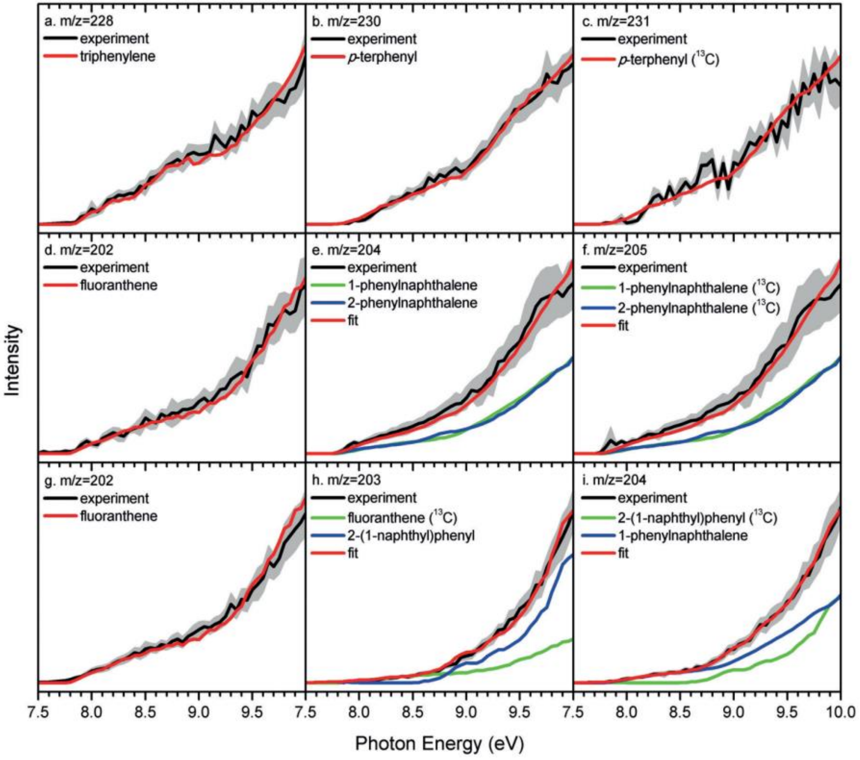
HACA was only found efficient for the ring growth from a triple fusing site of a PAH to produce symmetrical PAHs.

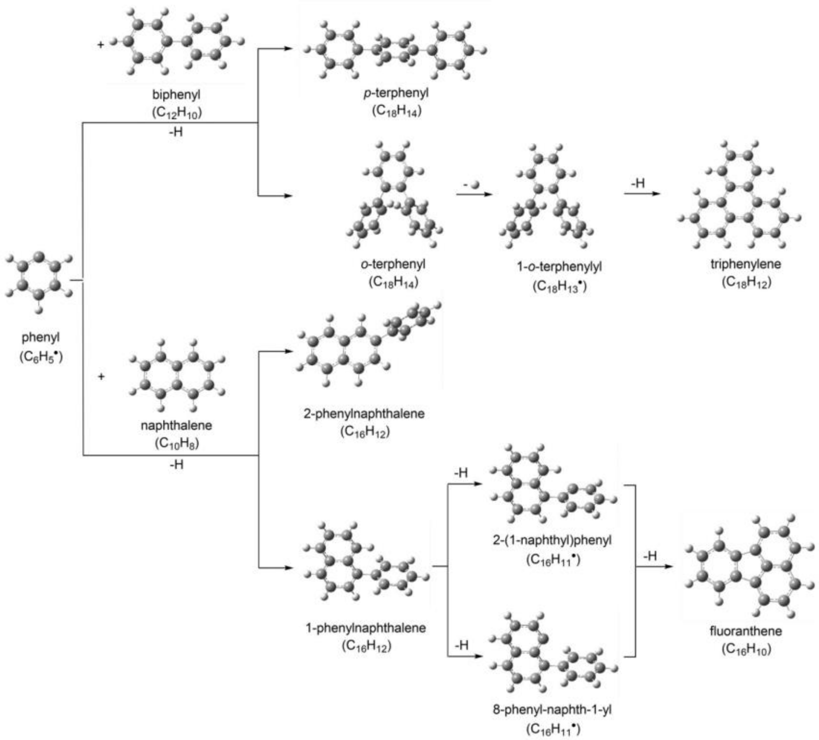
PAC was found efficient for ring growth from any fusing site of a PAH since it generates two new active sites in each step and can continue the endless growth

Collaboration of PAC with HACA was found important to meet the fastness of the soot formation process and also applicable to other combustion conditions

B. Shukla and M. Koshi, “A highly efficient growth mechanism of polycyclic aromatic hydrocarbons”, *Phys. Chem. Chem. Phys.*, **2010,** 12, 2427-2437

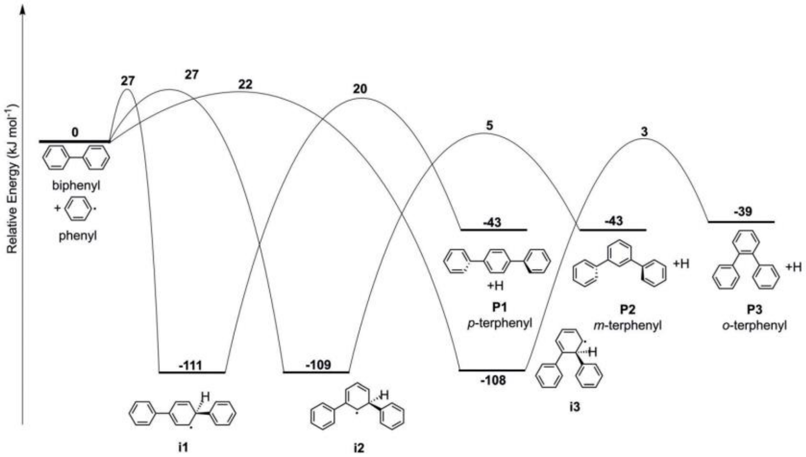
The role of phenyl radicals

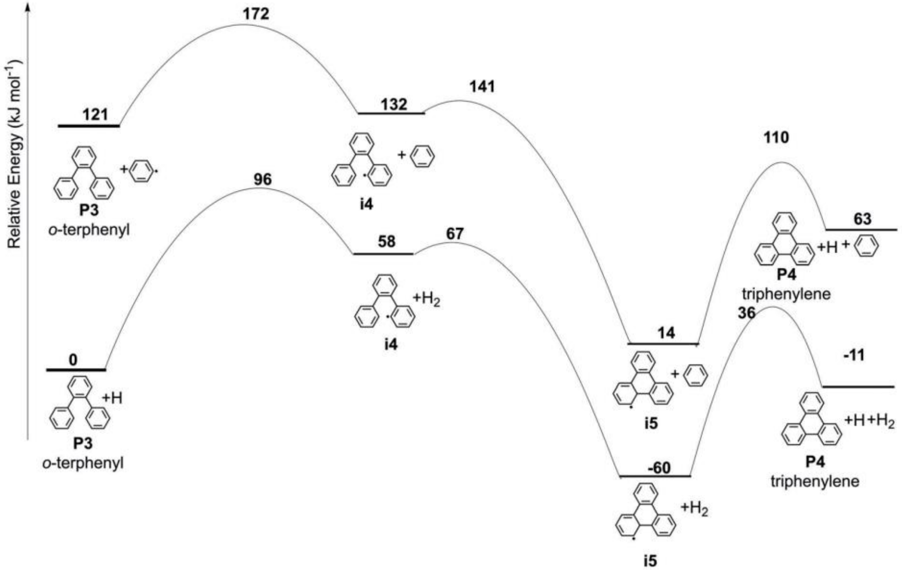




L. Zhao, "Synthesis of Polycyclic Aromatic Hydrocarbons by Phenyl Addition-Dehydrocyclization: The Third Way", *Angew. Chem. Int. Ed.*, **2019,** 131(48), 17603-17611

The role of phenyl radicals





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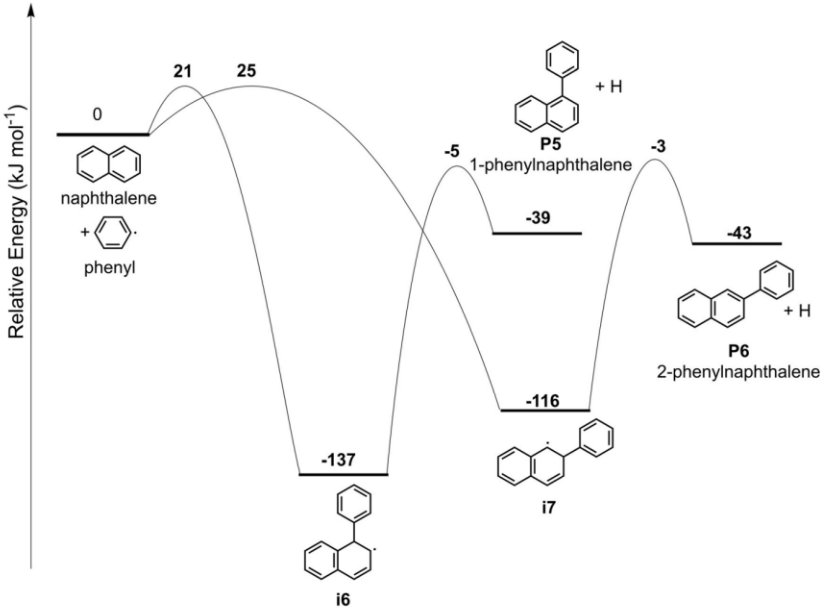
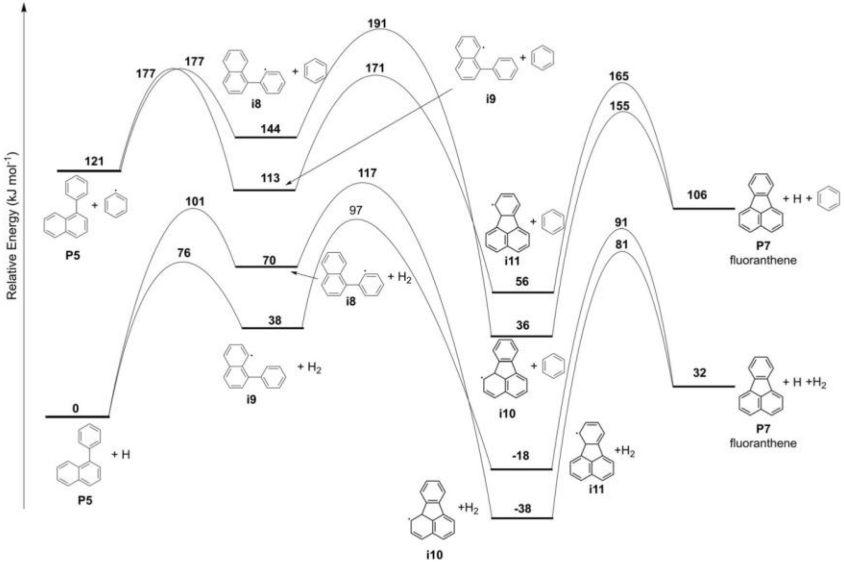
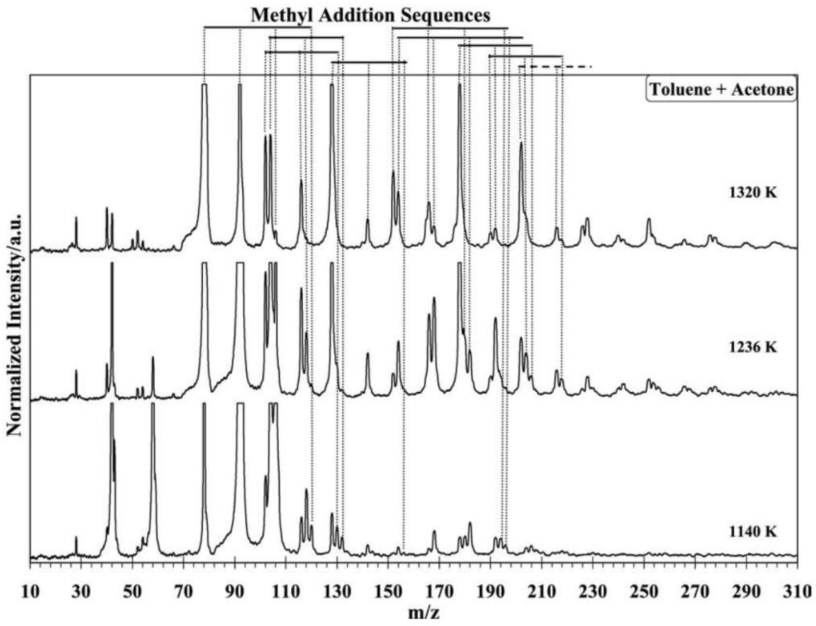
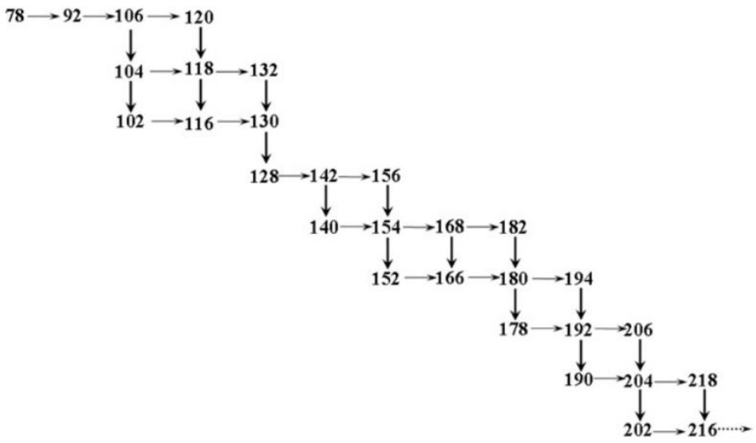




L. Zhao, “Synthesis of Polycyclic Aromatic Hydrocarbons by Phenyl Addition-Dehydrocyclization: The Third Way”, *Angew. Chem. Int. Ed.*, **2019,** 131(48), 17603-17611

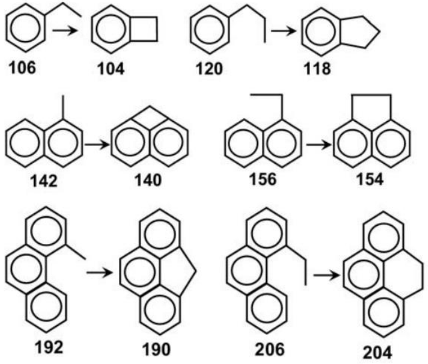
The role of methyl radicals

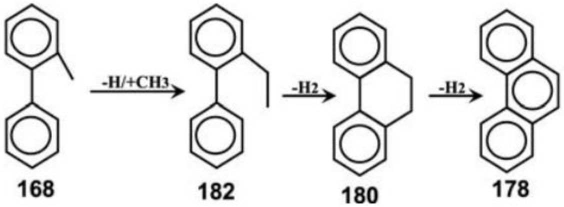


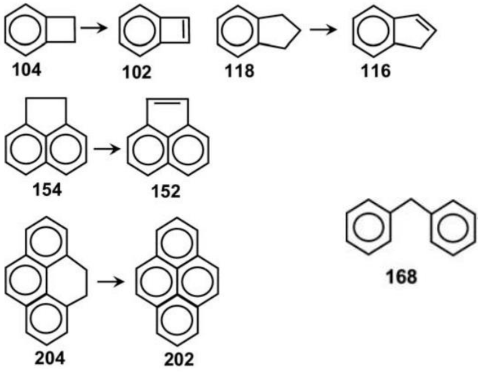


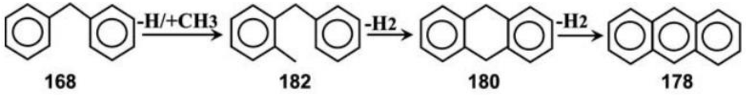
B. Shukla, A. Miyoshi, and M. Koshi, “Role of Methyl Radicals in the Growth of PAHs”, *J. Am. Soc. Mass Spectrom.*, **2010,** 21, 534-544

The role of methyl radicals





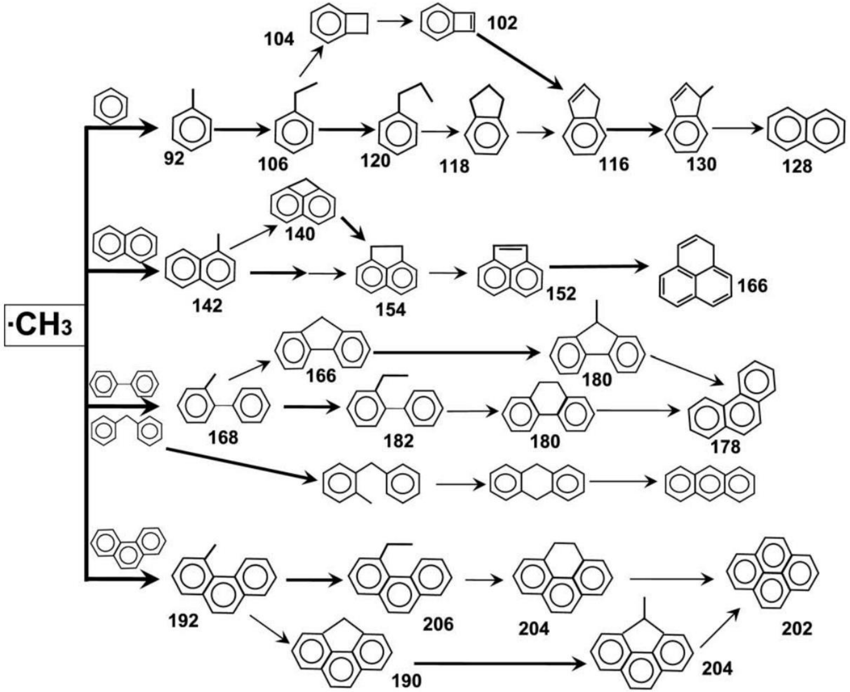




(19)

B. Shukla, A. Miyoshi, and M. Koshi, “Role of Methyl Radicals in the Growth of PAHs”, *J. Am. Soc. Mass Spectrom.*, **2010,** 21, 534-544

The role of methyl radicals



- A novel growth mechanism for PAHs, methyl addition/cyclization (MAC), has been proposed.
- The MAC mechanism was found to be capable of growing the sp2 network of carbons from any fusing site of a PAH, as well as growing CT and CP-PAH into benzenoid PAHs.
- The MAC mechanism is not as efficient as HACA or PAC in the rate of growth of PAHs
- Formation of three types of CP-PAHs indicates that cyclopentafused rings can be grown at single, double, and triple fusing sites
- Abstraction of hydrogen from a side chain with further addition of methyl radical was found to be preferable over hydrogen atom abstraction by methyl radical from the aromatic ring of alkyl aromatic compounds such as toluene

B. Shukla, A. Miyoshi, and M. Koshi, “Role of Methyl Radicals in the Growth of PAHs”, *J. Am. Soc. Mass Spectrom.*, **2010**, 21, 534-544

GAS PHASE CHEMICAL PHYSICS

Formation of Polycyclic Aromatic Hydrocarbons and Soot through the Eyes of a Chemist

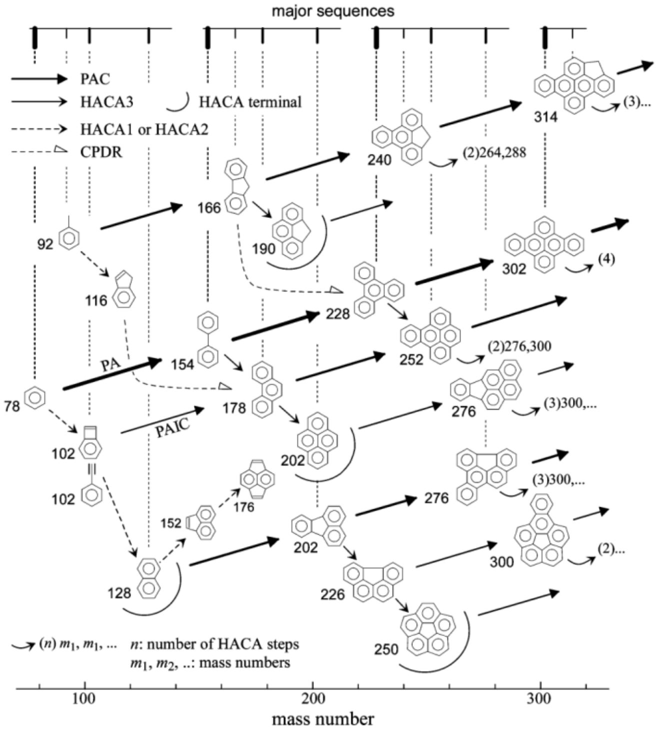
Lecture 7: Repetitive Pathways

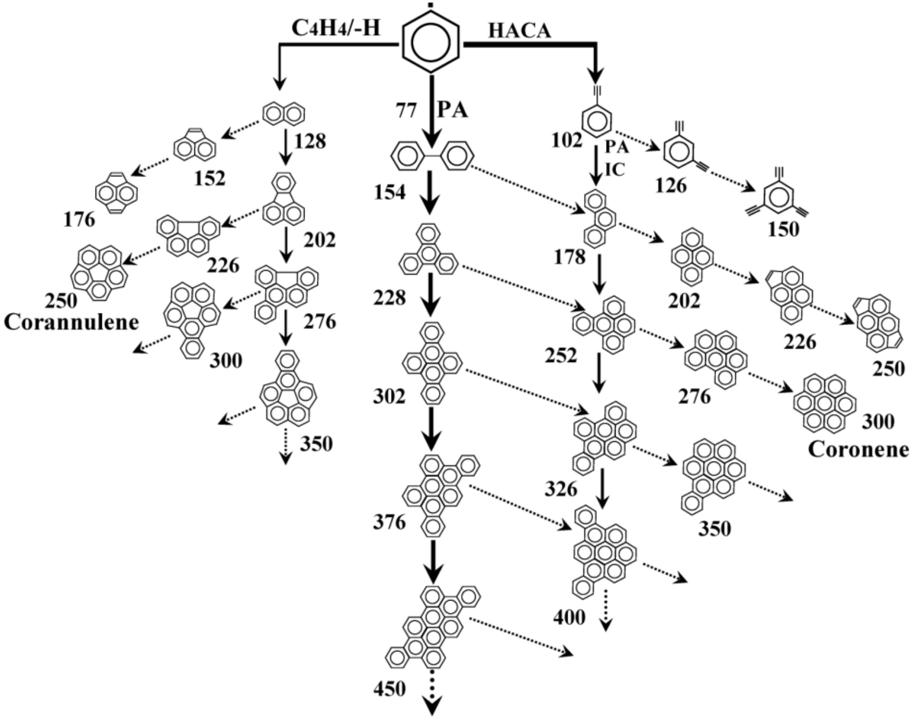
Nils Hansen

Sandia National Laboratories

COMBUSTION RESEARCH FACILITY
CRF
SANDIA NATIONAL LABORATORIES / CALIFORNIA

Repetitive Sequenzes



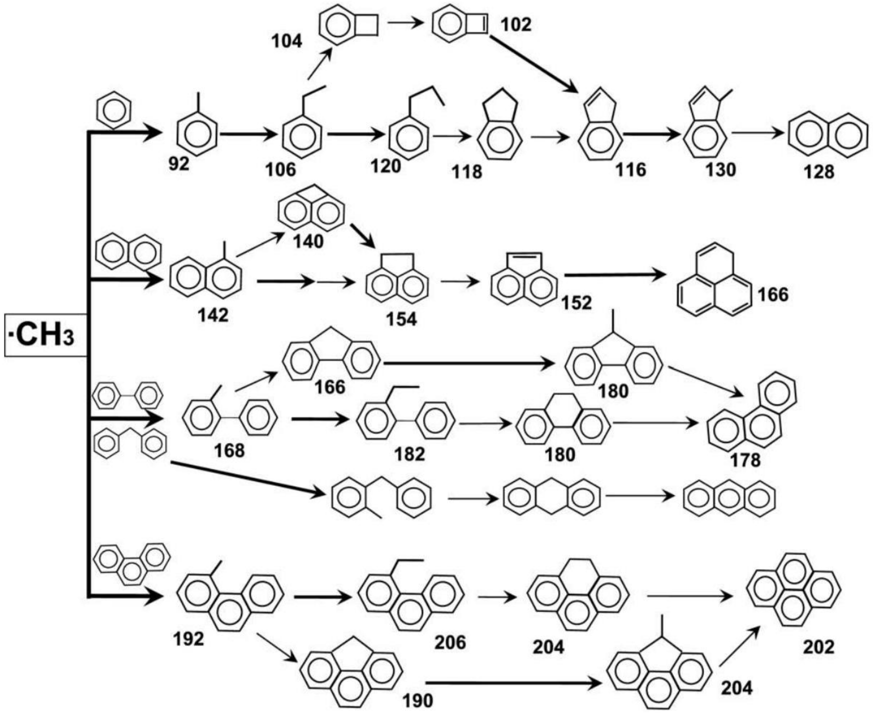


B. Shukla, A. Susa, A. Miyoshi, M. Koshi, *"Role of Phenyl Radicals in the Growth of Polycyclic Aromatic Hydrocarbons", J. Phys. Chem. A,* **2008,** 112, 2362-2369

B. Shukla and M. Koshi, *"A highly efficient growth mechanism of polycyclic aromatic hydrocarbons", Phys. Chem. Chem. Phys.,* **2010,** 12, 2427-2437

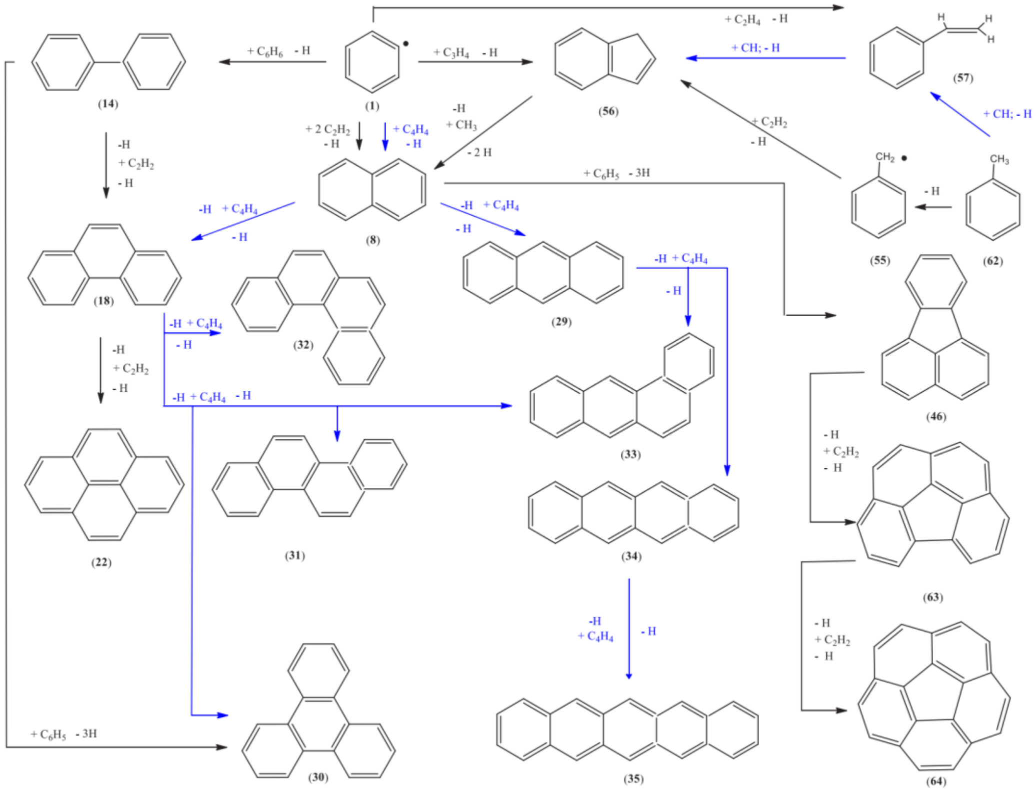
GAS PHASE CHEMICAL PHYSICS

Repetitive Sequenzes



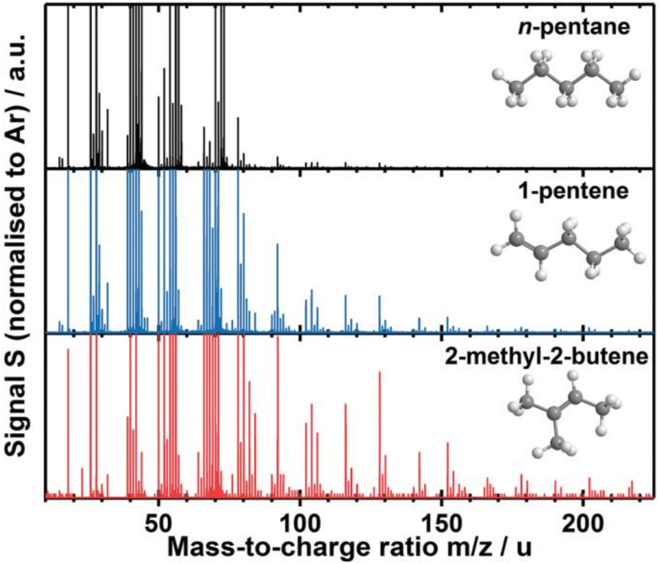
B. Shukla, A. Miyoshi, and M. Koshi, *"Role of Methyl Radicals in the Growth of PAHs", J. Am. Soc. Mass Spectrom.*, **2010,** 21, 534-544

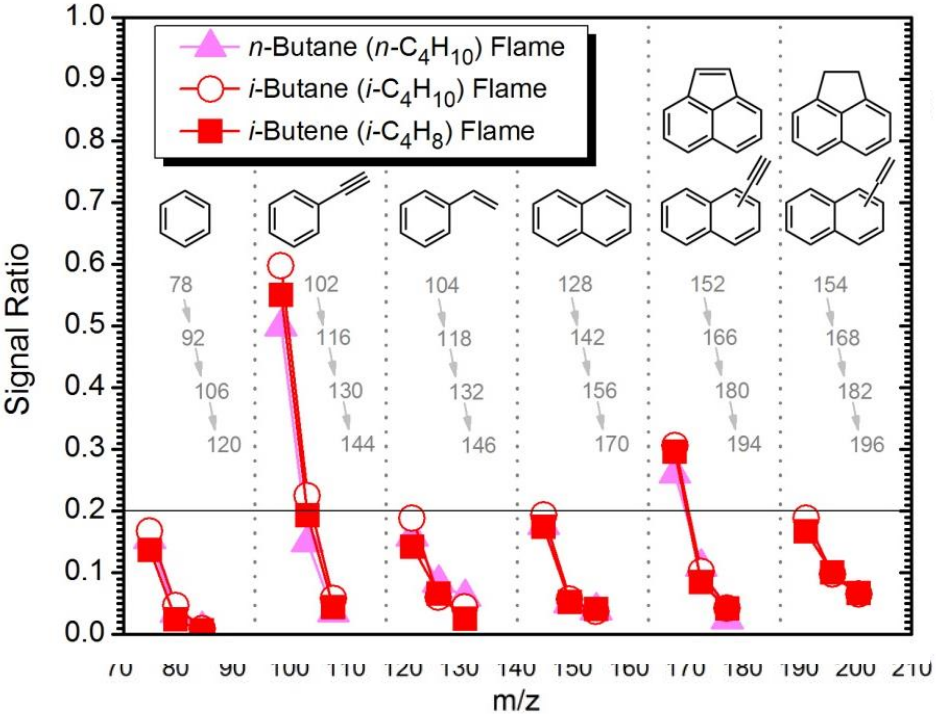
Repetitive Sequenzes



R. I. Kaiser and N. Hansen, *"An Aromatic Universe – A Physical Chemistry Perspective"*, *J. Phys. Chem. A*, **2021,** 125, 3826-3840

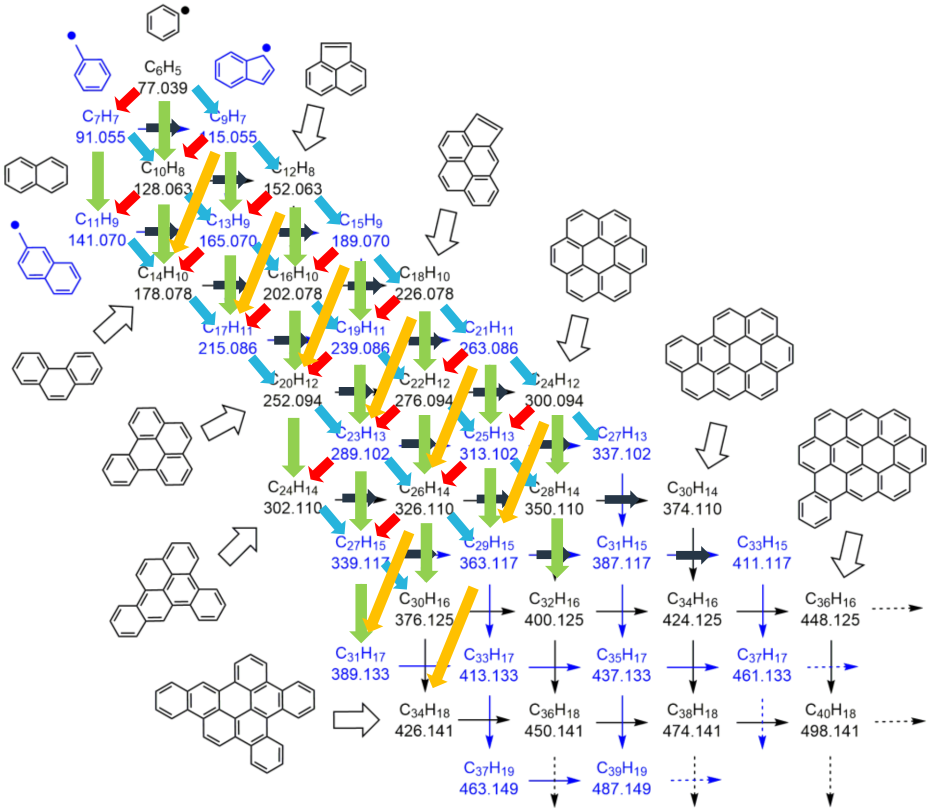
Molecular-Growth From The First Aromatic Ring to Pyrene





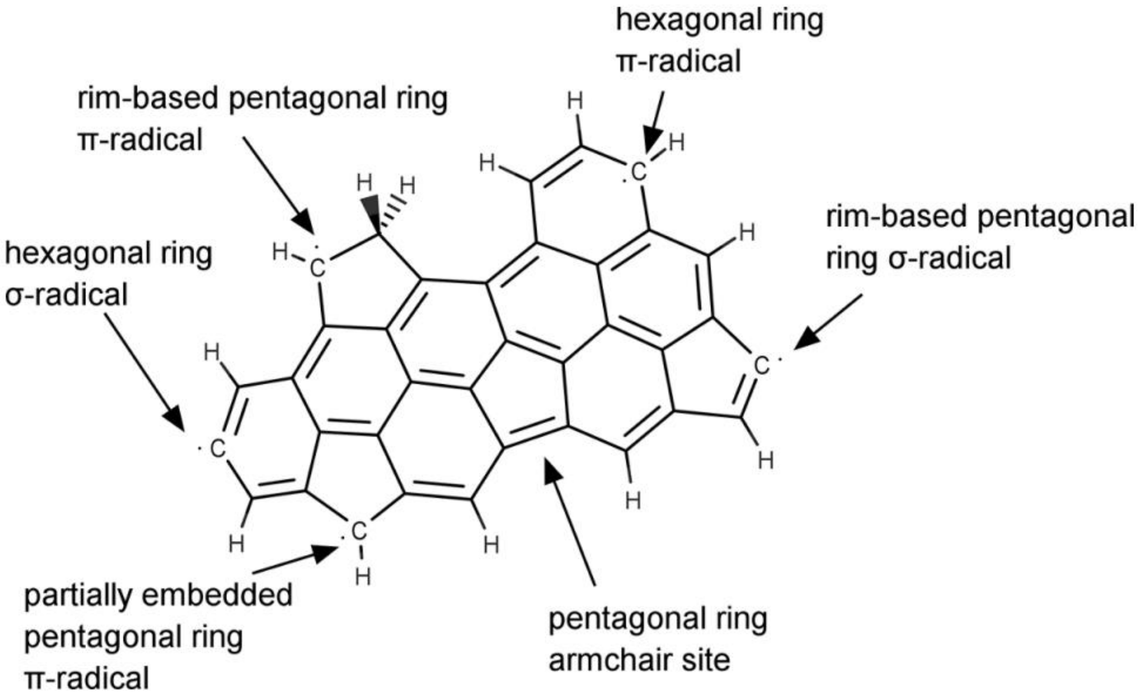
N. Hansen *et al., Combust. Flame,* **2017,** 180, 250-261
L. Ruwe *et al., Combust. Flame,* **2017,** 175, 34-46 and *Phys. Chem. Chem. Phys.,* **2018,** 20, 10780-10795

Identification of Main Reaction Pathways:



B. D. Adamson, S. A. Skeen, M. Ahmed, N. Hansen, *J. Phys. Chem. A,* **2018,** 122(48), 9338-9349

Aromatic site description of PAHs


hexagonal ring

π-radical

rim-based pentagonal ring

π-radical

hexagonal ring

σ-radical

rim-based pentagonal

ring σ-radical

partially embedded

pentagonal ring

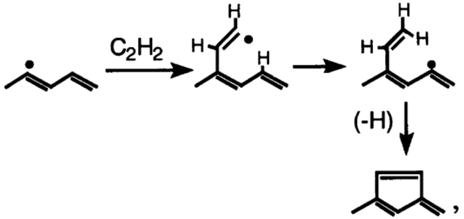
π-radical

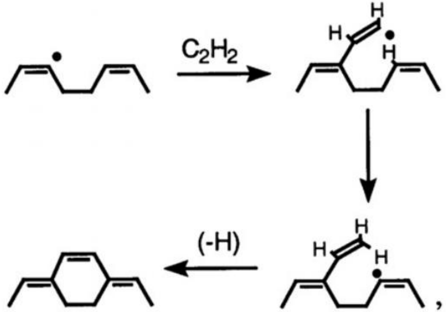
pentagonal ring

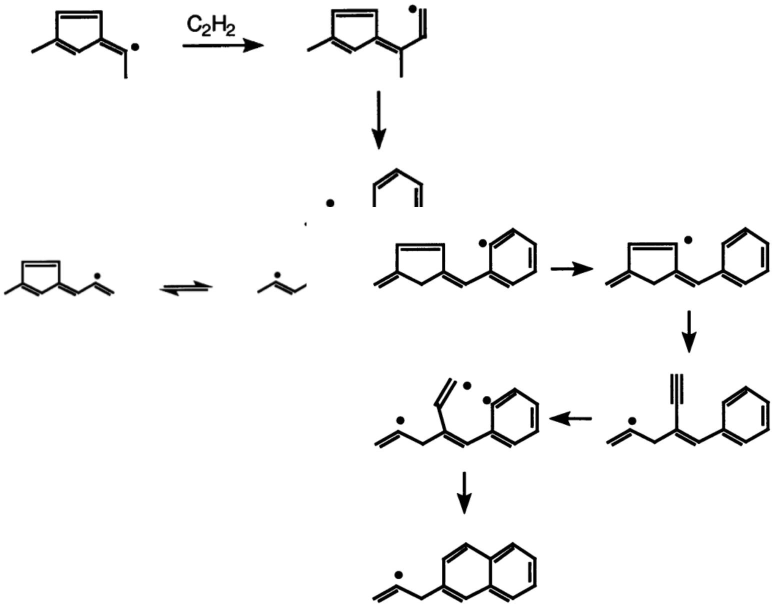
armchair site

J. W. Martin et al., “Soot inception: Carbonaceous nanoparticle formation in flames”, *Progr. Combust. Energy Sci.*, **2022,** 88, 100956

Aromatic site description of PAHs

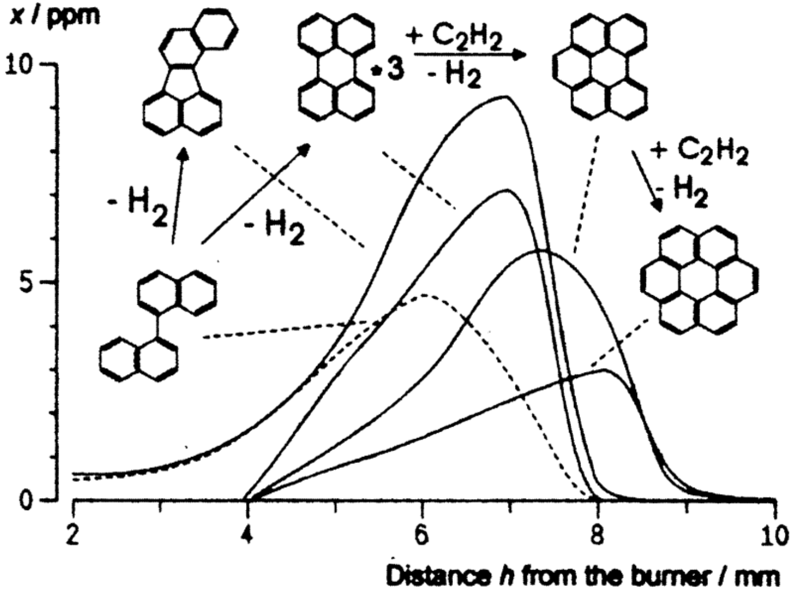






M. Frenklach, “Reaction mechanism of soot formation in flames”, *Phys. Chem. Chem. Phys.*, **2002,** 4, 2028-2037

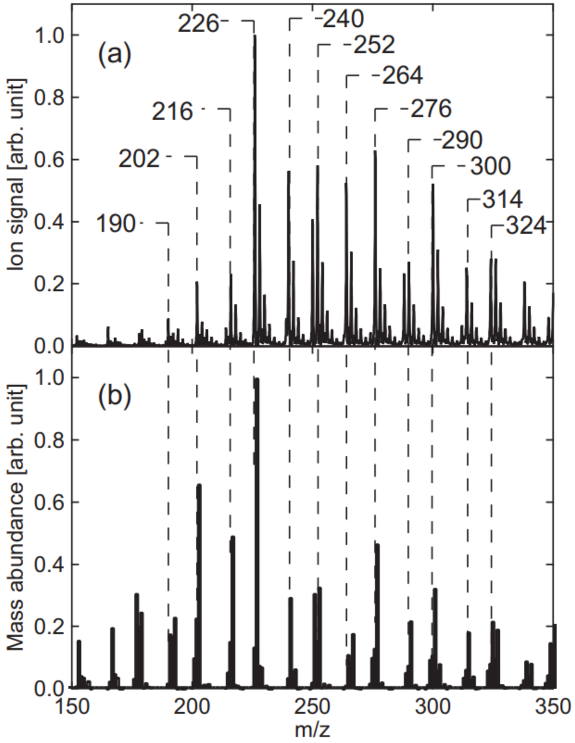
Aromatic site description of PAHs

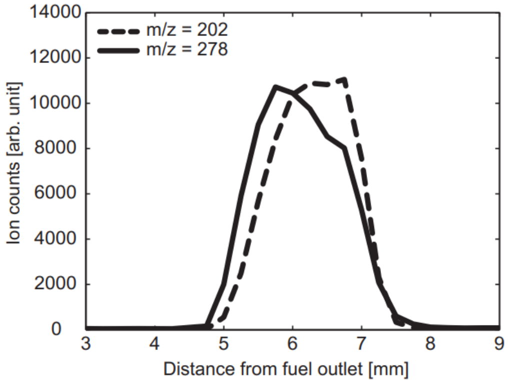


J. Griesheimer, K.-H. Homann, "Large molecules, radicals ions, and small soot particles in fuel-rich hydrocarbon flames. Part II. Aromatic radicals and intermediate PAHs in a premixed low-pressure naphthalene/oxygen/argon flame", *Proc. Combust. Inst.,* **1998,** 27, 1753-1759

GAS PHASE CHEMICAL PHYSICS

Aromatic site description of PAHs

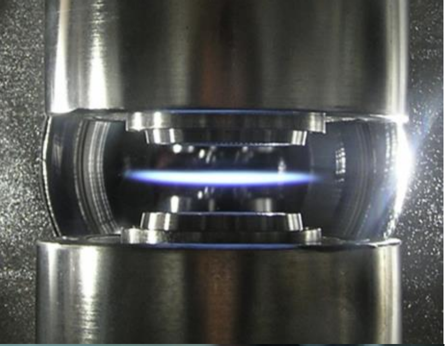


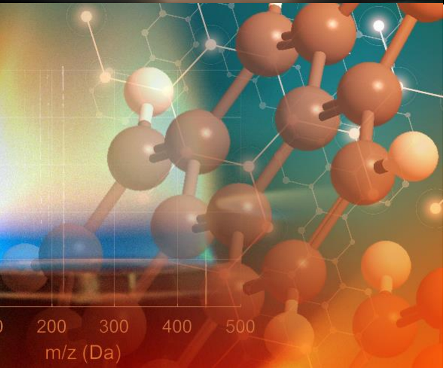


The experimental results demonstrate that species of higher masses can build up concentration ahead of species of lower masses.

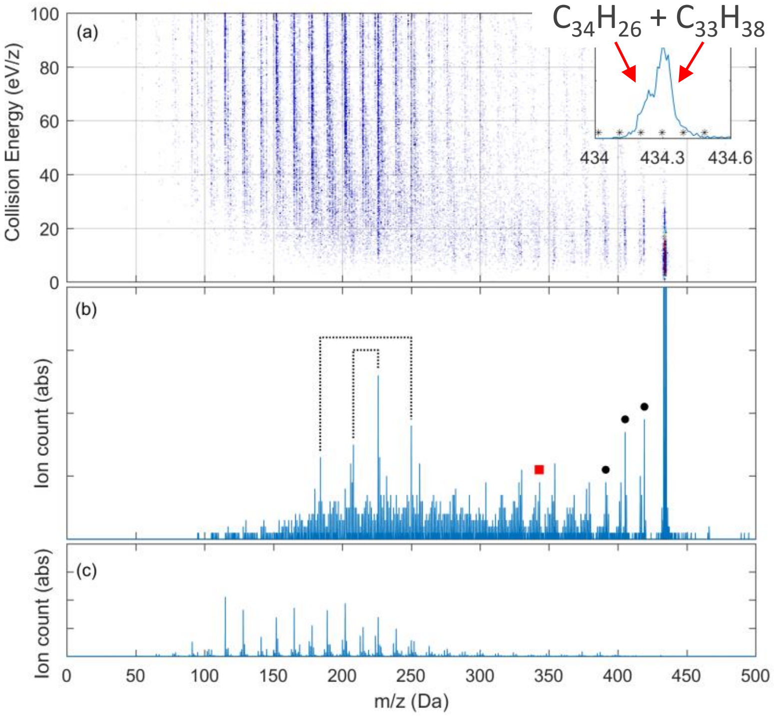
The results show, for example, that the peak at m/z = 278 rises ahead of the peak at m/z = 202, the latter corresponding to the mass at which pyrene is traditionally expected to be present

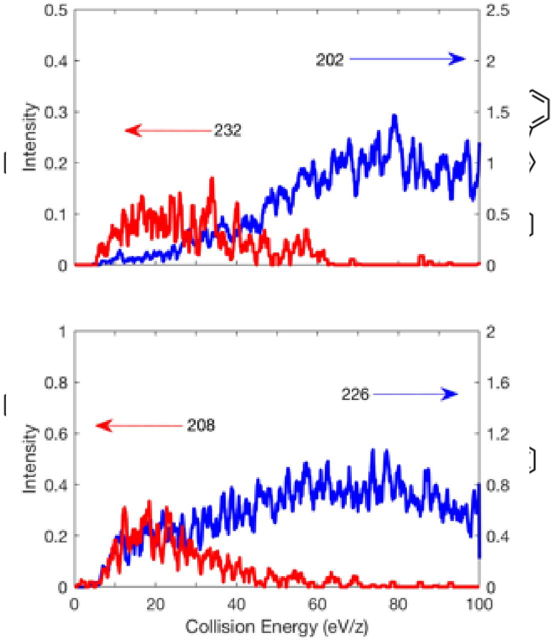
K. O. Johansson *et al.*, “Soot precursor formation and limitations of the stabilomer grid”, *Proc. Combust. Inst.*, **2015,** 35, 1819-1826





Tandem Mass Spectrometry (MS-MS Mode): Identification of aliphatically bridged PAHs





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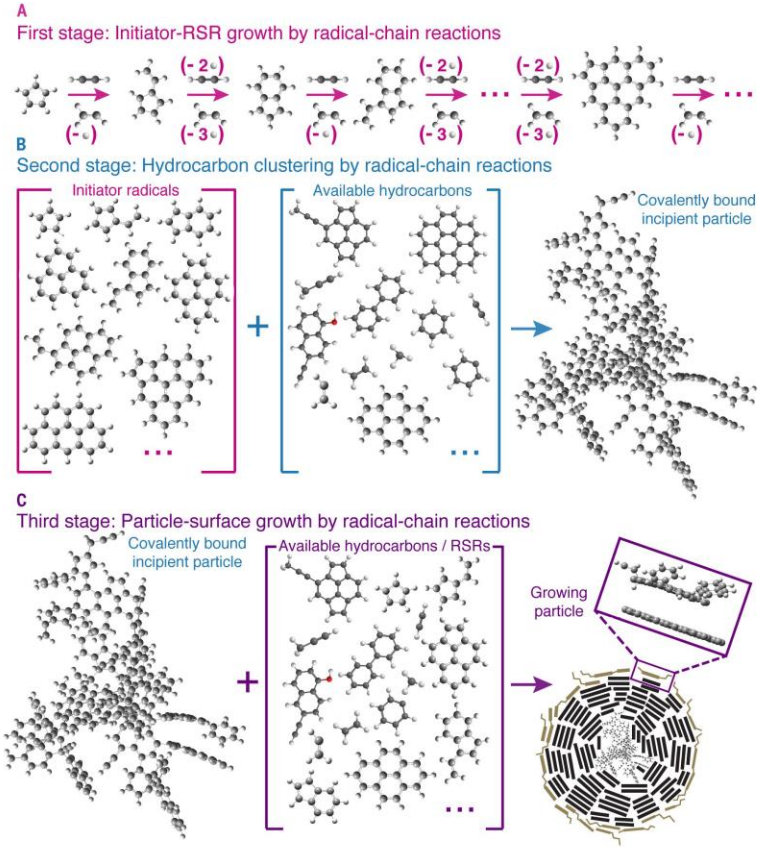
Radical Chain Reactions

- Radical Chain Reactions have been proposed to be key to the formation of polycyclic aromatic hydrocarbons (PAHs) and soot.

- Johansson *et al.* proposed the **“Clustering of Hydrocarbons by Radical Chain Reactions (CHRCR)”** mechanism



Johansson *et al.*, *Science*, **2018,** 361, 997–1000

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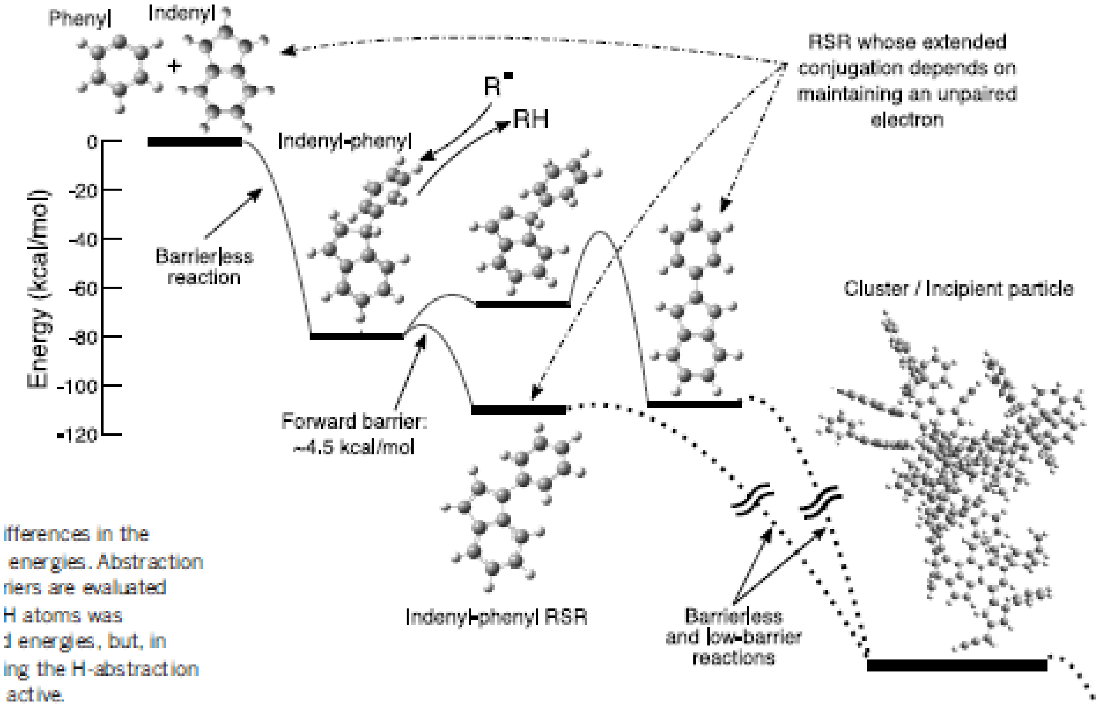
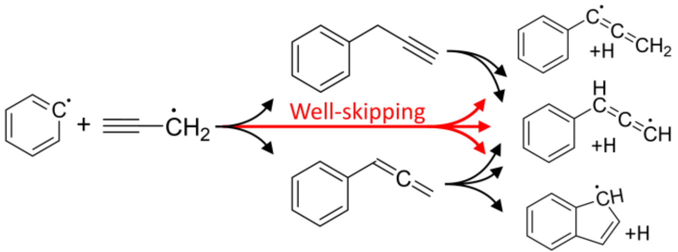
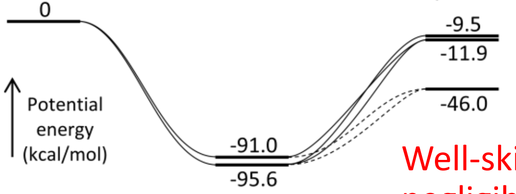


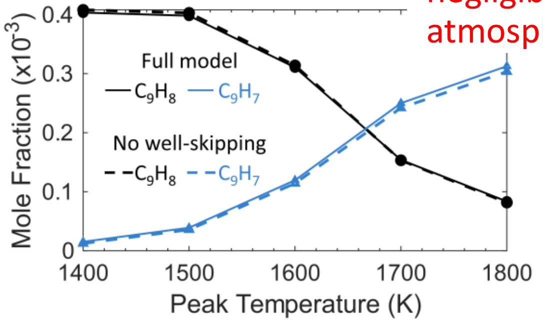
ifferences in the
energies. Abstraction
riers are evaluated
H atoms was
d energies, but, in
ing the H-abstraction
active.

Johansson *et al., Science,* **2018,** 361, 997–1000

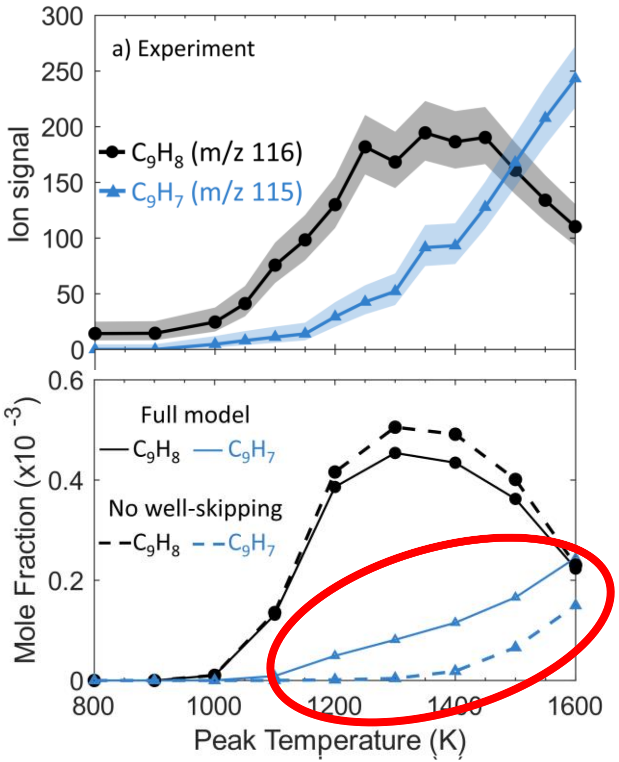
Phenyl + Propargyl







Well-skipping is negligible at atmospheric pressure!



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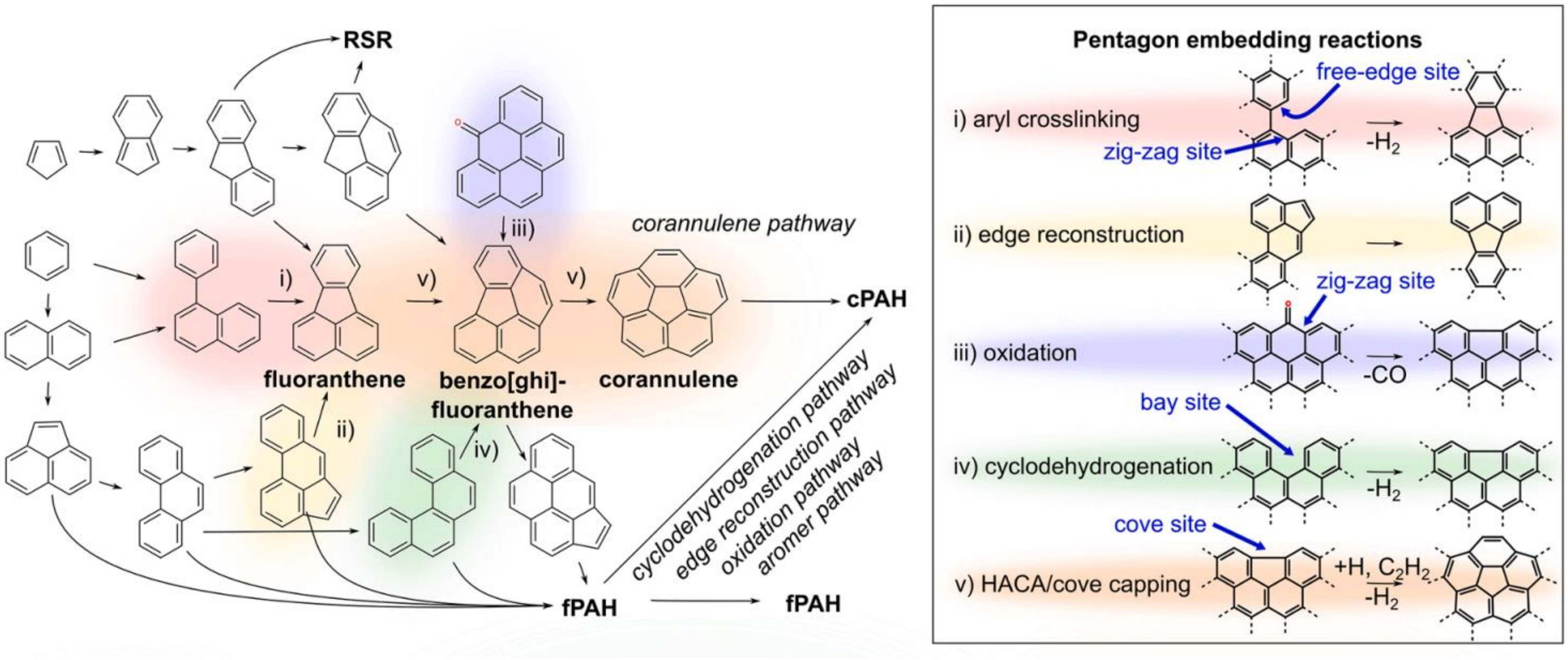
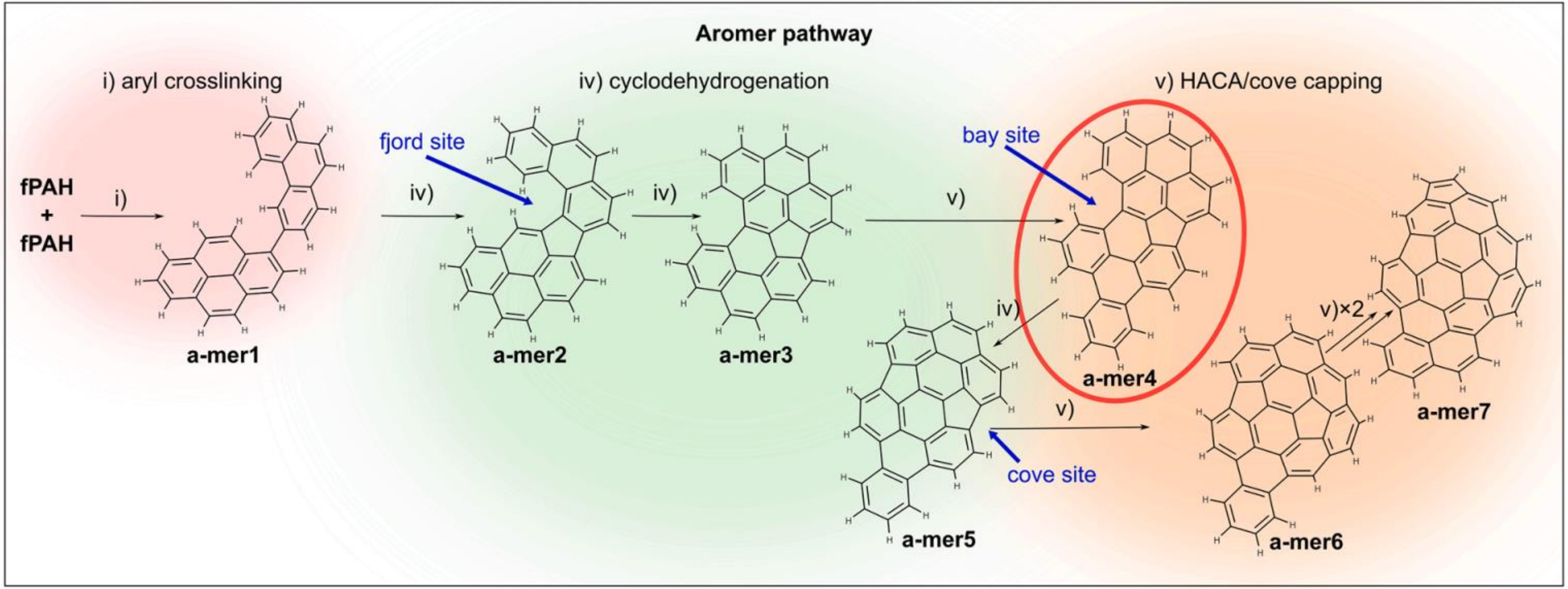
Curvature Integration



J. W. Martin et al., “Soot inception: Carbonaceous nanoparticle formation in flames”, *Progr. Combust. Energy Sci.*, **2022**, 88, 100956

Curvature Integration



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清华大学燃烧能源中心

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