



Chemical Kinetics of Combustion Processes

Hai Wang

B. Yang, J. Camacho, S. Lieb, S. Memarzadeh,
S.-K. Gao and S. Koumlis

University of Southern California

Benzene + O(³P) → Products

- Overall rate coefficient extensively studied, but the products and branching ratios not well known.
- Theoretical challenges in dealing with spin-state crossing.
- Product distributions determined over 300 to 1000 K and 1 to 10 Torr (with Taatjes/Sandia).
- Cyclopentadiene was directly identified for the first time, in addition to phenol and phenoxy.
- ab initio calculations (with Krylov/ USC) and master equation/RRKM modeling for data extrapolation.

Taatjes, C. A., Osborn, D. L., Selby, T. M., Meloni, G., Trevitt, A. J., Epifanivskii, E. Krylov, A. I., Sirjean, B., Dames, E., Wang, H. "Products of the benzene + O(³P) reaction," *Journal of Physical Chemistry A*, 114, 3355-3370 (2010)

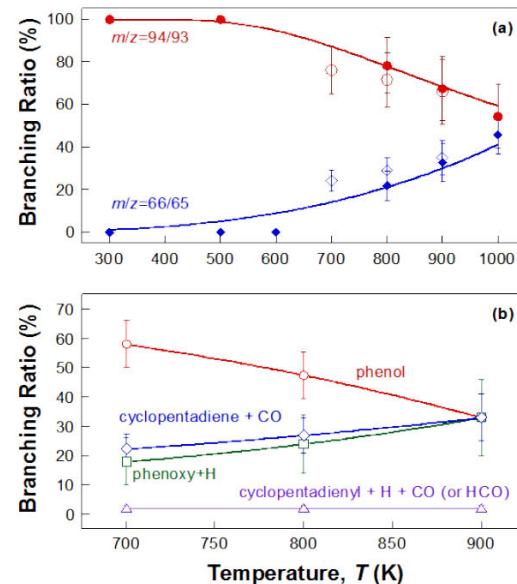
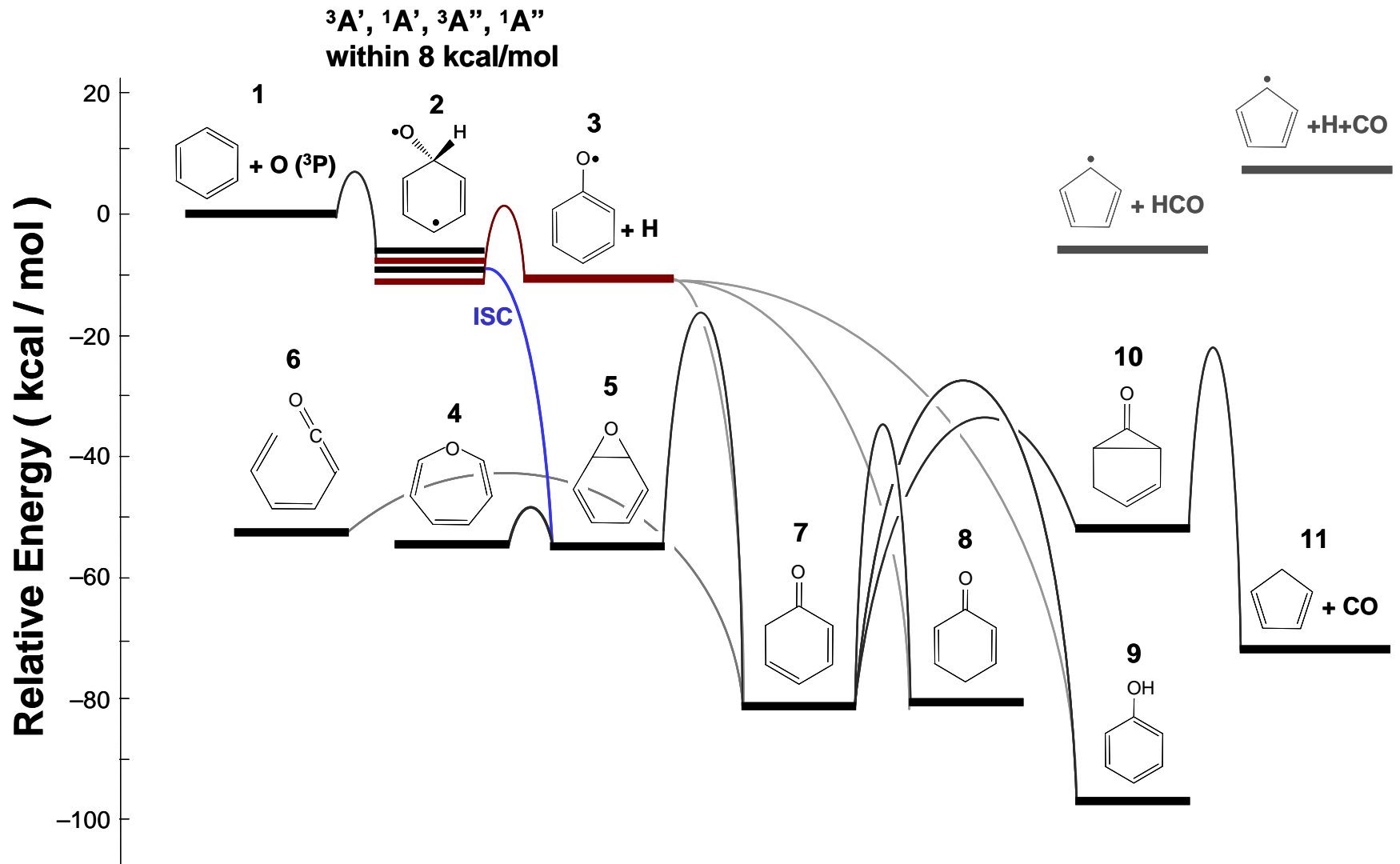


Figure 1. Branching ratios observed as a function of temperature at 4 Torr for (a) $m/z=94/93$ and $m/z=66/65$ by magnetic sector mass spectrometer (filled symbols) and time-of-flight mass spectrometer (open symbols), and (b) branching ratios determined by time-of-flight mass spectrometer. Lines are drawn to guide the eye. Error bars are 2σ -standard deviations.

Benzene + O(³P) → Products



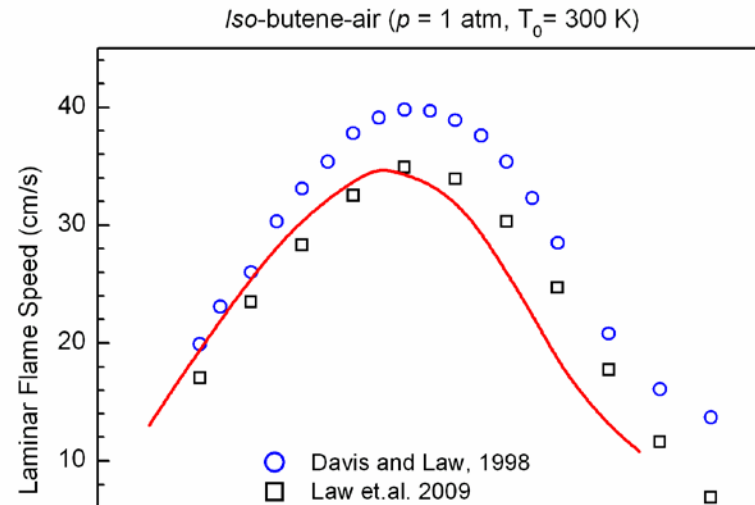
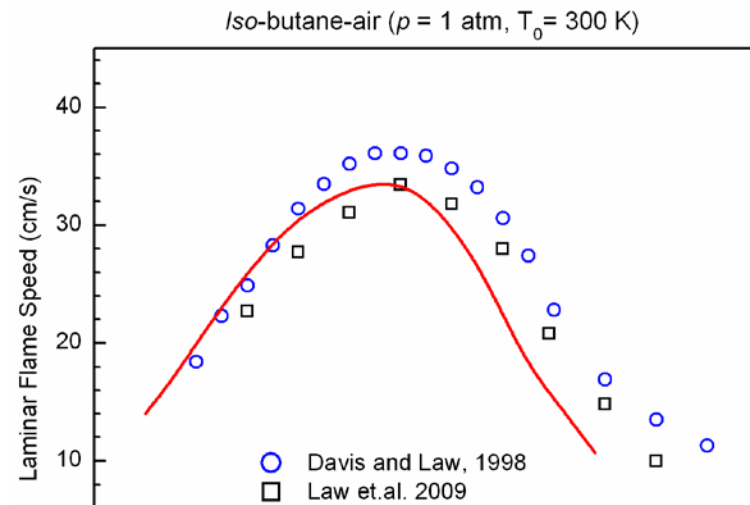
Benzene + O(³P) → Products

Table 6. Branching ratios experimentally determined and computed for reaction R1.

Reaction channel	<i>P</i> (Torr)	<i>T</i> (K)	Branching ratio	
			Experimental	Computational
C ₆ H ₅ OH (9)	4	700	0.58 ± 0.08 ^a	0.56 (0.65) ^d
	4	800	0.47 ± 0.08 ^a	0.43 (0.50) ^d
	4	900	0.33 ± 0.08 ^a	0.29 (0.37) ^d
	10	800	0.59 ± 0.08 ^a	0.51 (0.61) ^d
	10	900	0.41 ± 0.09 ^a	0.40 (0.49) ^d
C ₆ H ₅ O• (3) + H•	4	700	0.18 ± 0.08 ^a	0.18
	4	800	0.24 ± 0.10 ^a	0.21
	4	900	0.33 ± 0.13 ^a	0.23
	10	800	0.19 ± 0.09 ^a	0.21
	10	900	0.28 ± 0.12 ^a	0.23
C ₅ H ₆ (11) + CO	4	700	0.22 ± 0.05 ^a	0.17
	4	800	0.27 ± 0.06 ^a	0.29
	4	900	0.33 ± 0.08 ^a	0.40
	10	800	0.21 ± 0.05 ^a	0.18
	10	900	0.27 ± 0.07 ^a	0.28

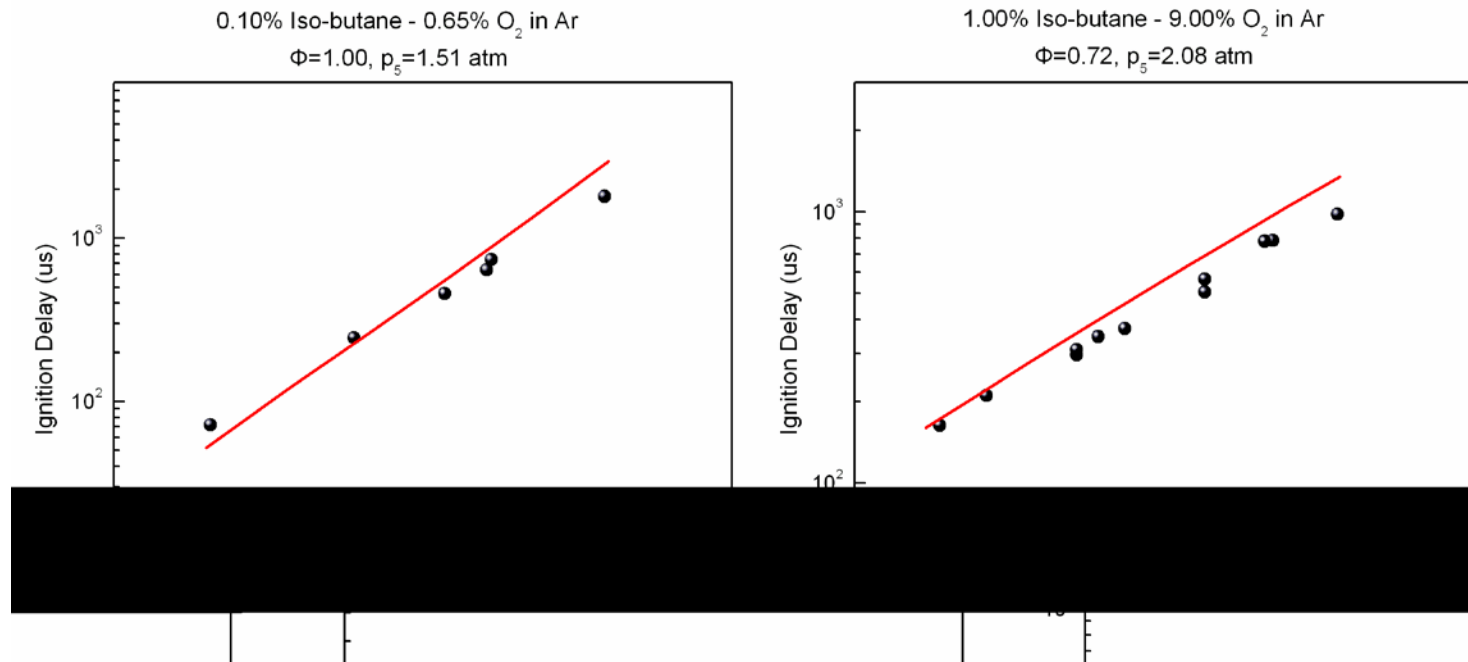
Kinetic Modeling Studies of Iso-butane and Iso-butene Combustion (work-in-progress)

- Chemical kinetic submodel of iso-butanol combustion.
- In collaboration with N. Hansen/Sandia through Bin Yang (roving postdoc).
- A total of 61 datasets considered, including two burner stabilized flames (30 Torr) probed by Synchrotron Photoionization Molecular Beam Mass Spectrometry (Hansen/Yang).
- Preliminary results show that USC Mech II behaves rather well against the data, but improvements are needed for the initial pyrolysis and oxidation of isobutane and isobutene.



Kinetic Modeling Studies of Iso-butane and Iso-butene Combustion (work-in-progress)

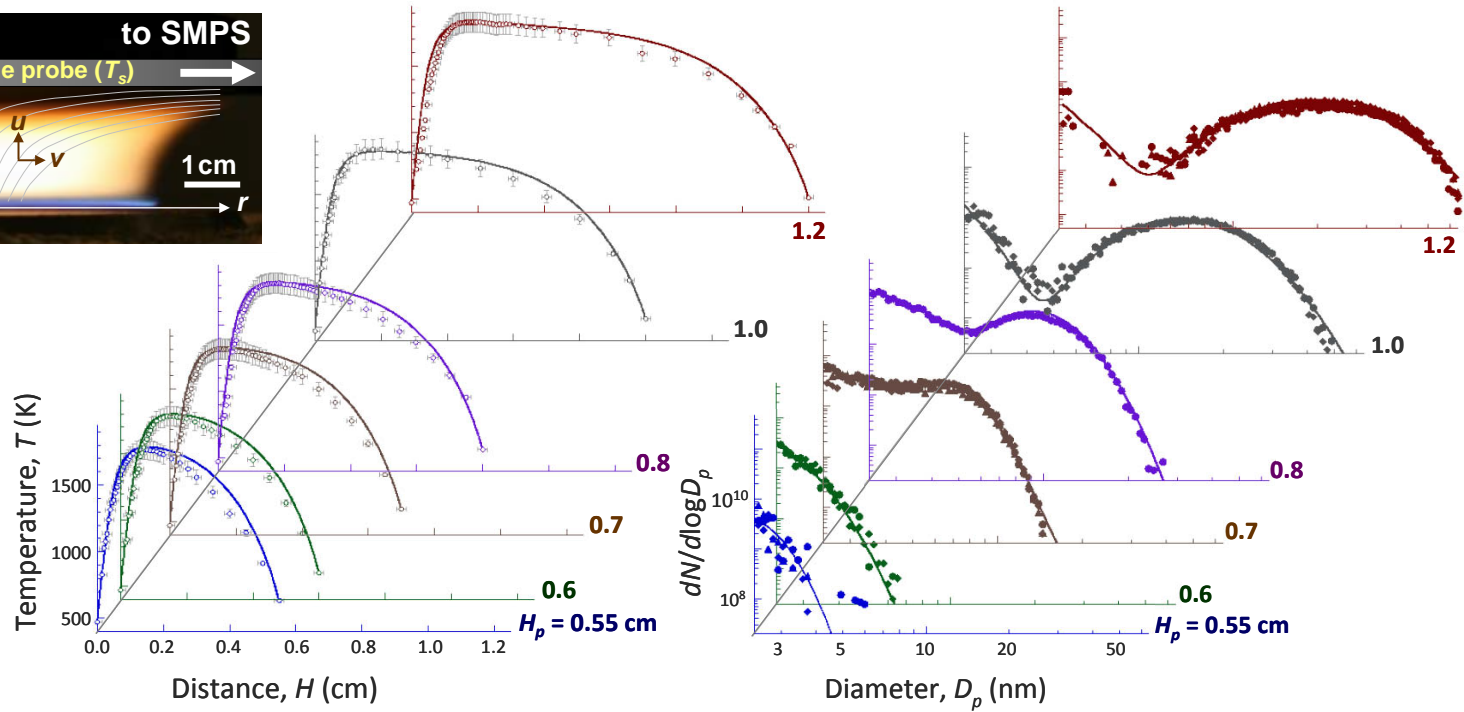
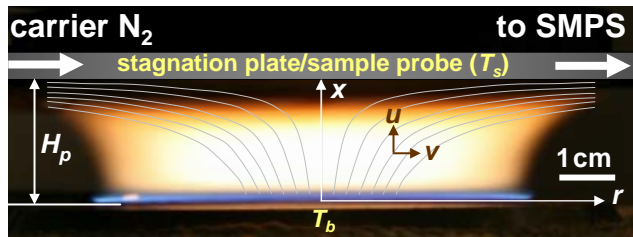
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Sooting Behaviors of *n*- and *iso*-Butanol Flames (Work-in-Progress)

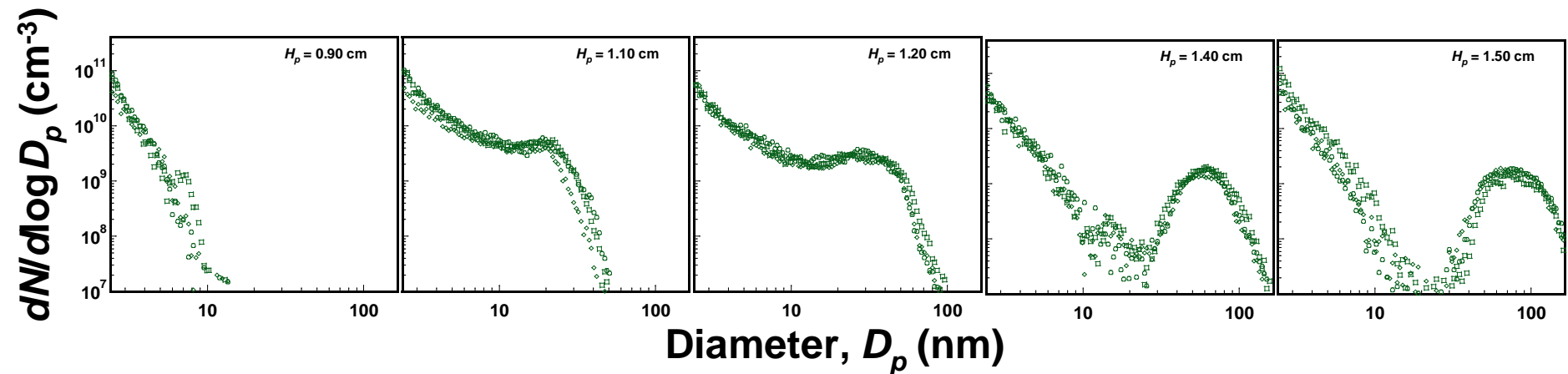
- Fuel-rich chemistry and sooting behaviors of butanol isomers are unknown.
- Soot formation characterized in burner-stabilized stagnation flames.

Burner-stabilized stagnation flame approach



Sooting Behaviors of *n*- and *iso*-Butanol Flames (Work-in-Progress)

- Fuel-rich chemistry and sooting behaviors of butanol isomers are unknown.
- Soot formation characterized in burner-stabilized stagnation flames.
- No significant difference between *n*-butanol and isobutanol in particle inception and soot mass growth.
- Soot formed show a strong and persistent nucleation behavior well into the post flame.
- In comparison to comparable ethylene flames, soot inception in butanol flames takes substantially longer reaction time, but once nucleation starts, surface reaction is as fast as the ethylene flames.



PAH Precursor Chemistry (1)

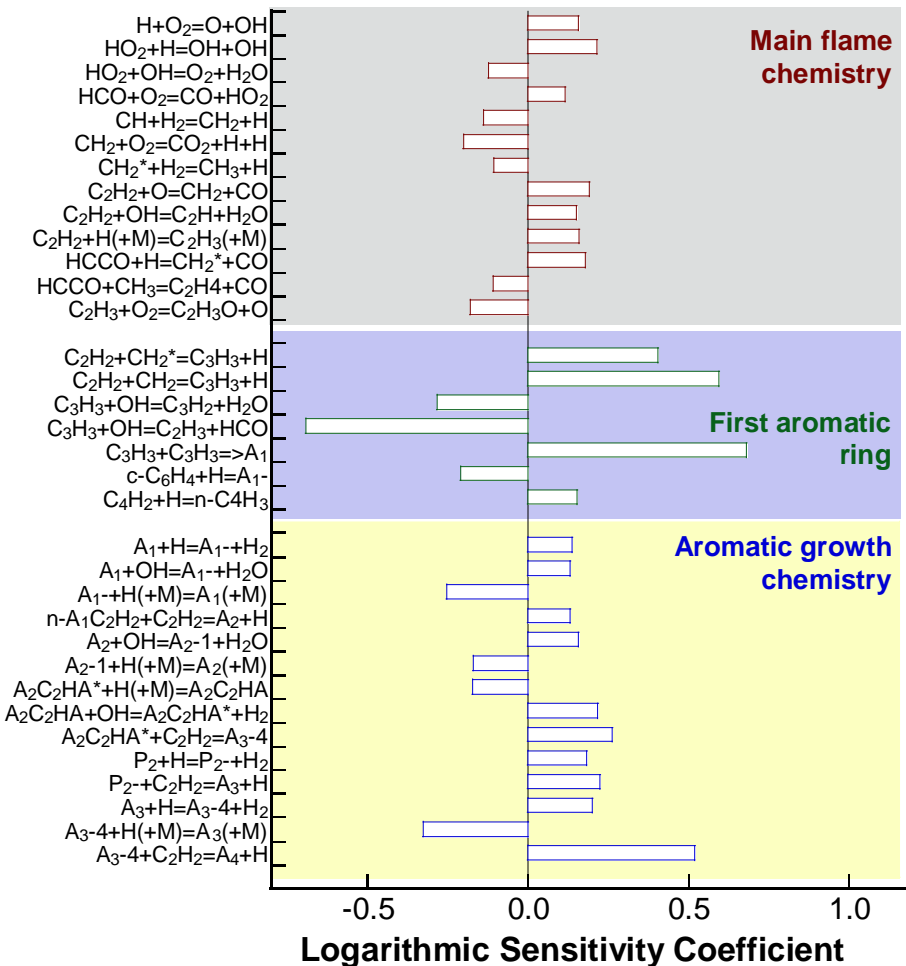
PAH formation is sensitive to a multitude of elementary reactions and local flame conditions.

Accurate prediction of PAH formation may require a precision in main flame chemistry currently unavailable.

PAH formation can be highly sensitive to fuel structures.

Possibly a large number of pathways to PAHs have yet been considered.

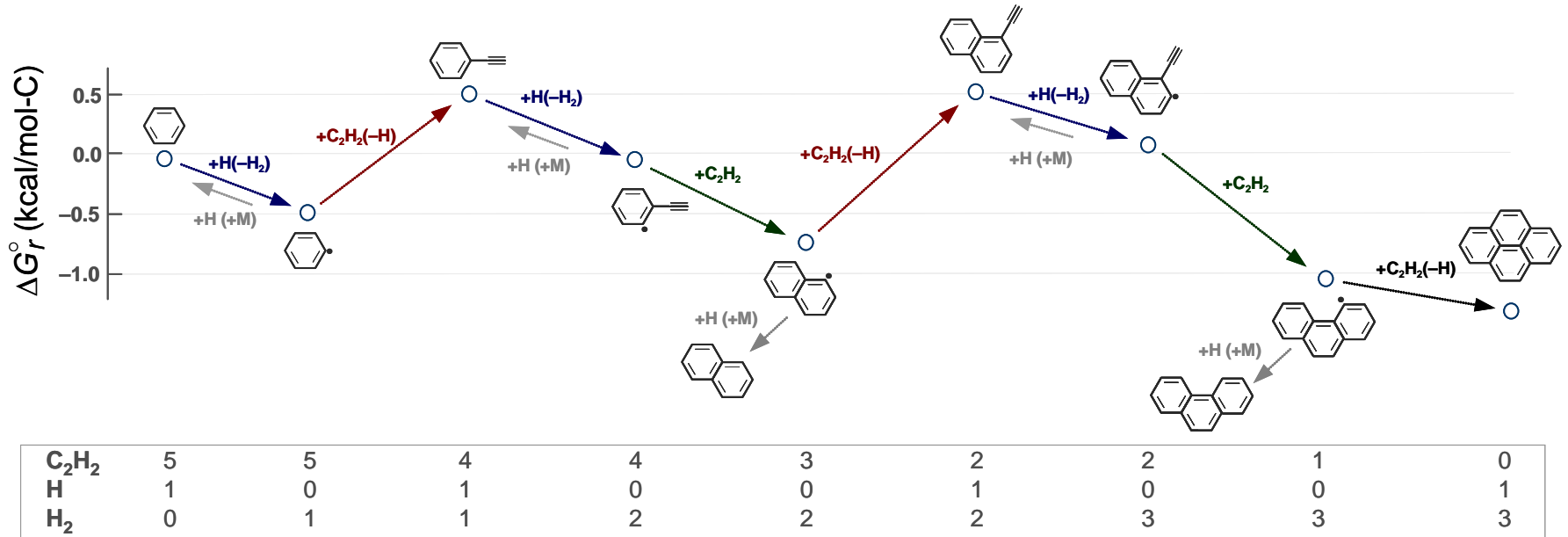
Spectral sensitivity of pyrene concentration
90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame
(Bockhorn), $H = 0.55$ cm



Wang & Frenklach, C&F (1997)

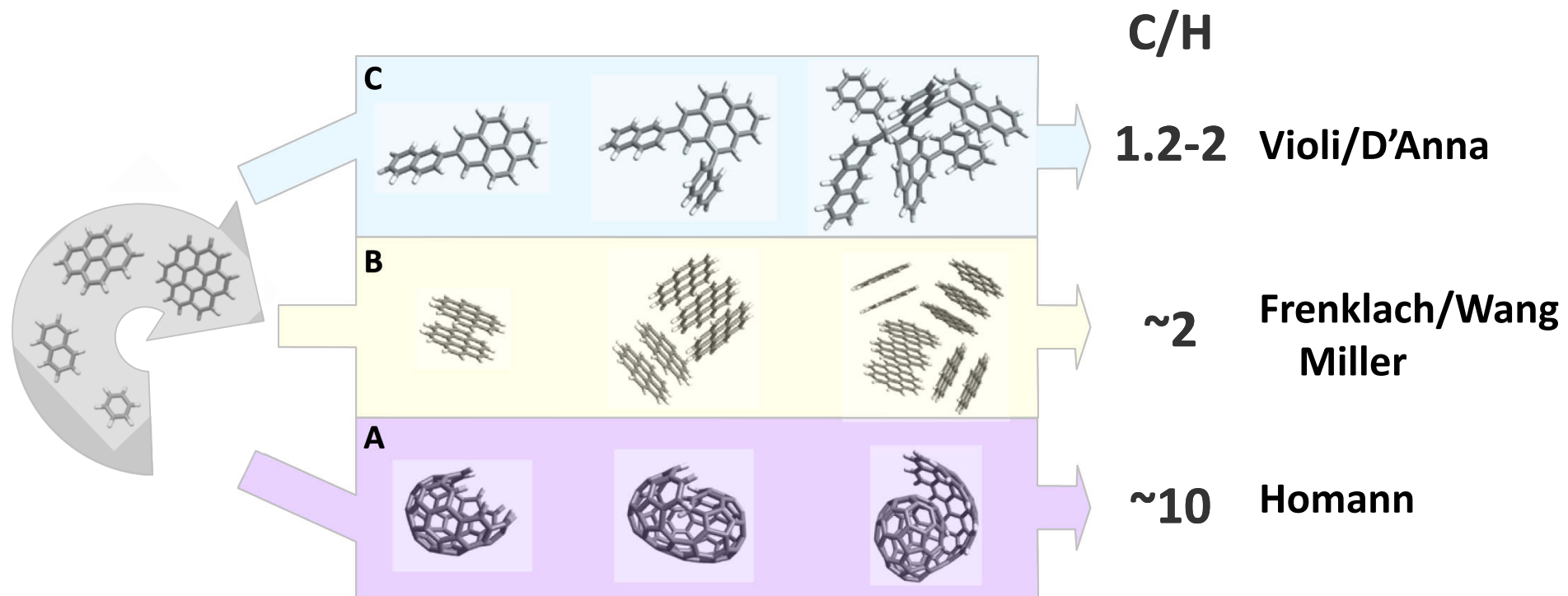
PAH Precursor Chemistry (2)

Thermokinetic Origin of PAH Formation/Growth Beyond HACA

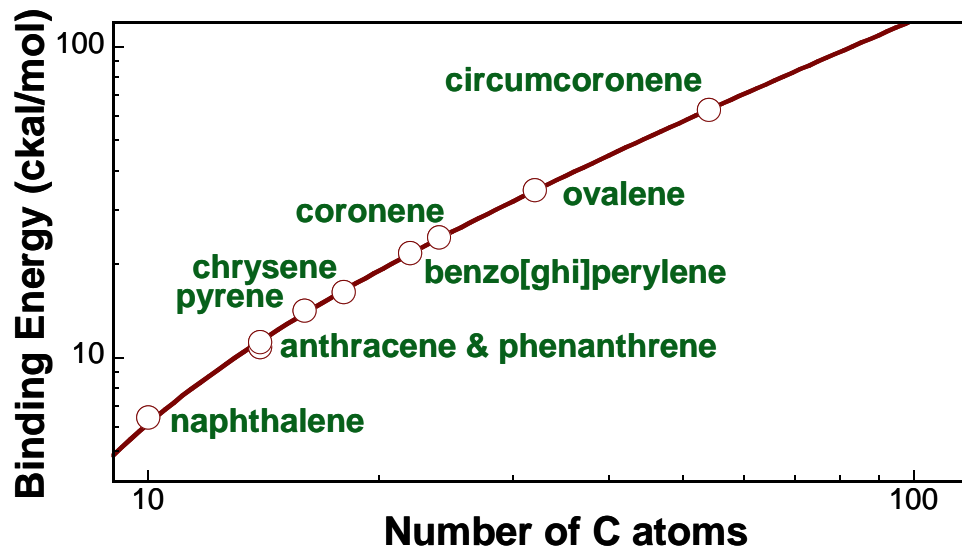


- While HACA captures the thermokinetic requirements for PAH formation, its reversibility opens it to competitions from other pathways

Soot Nucleation (1)

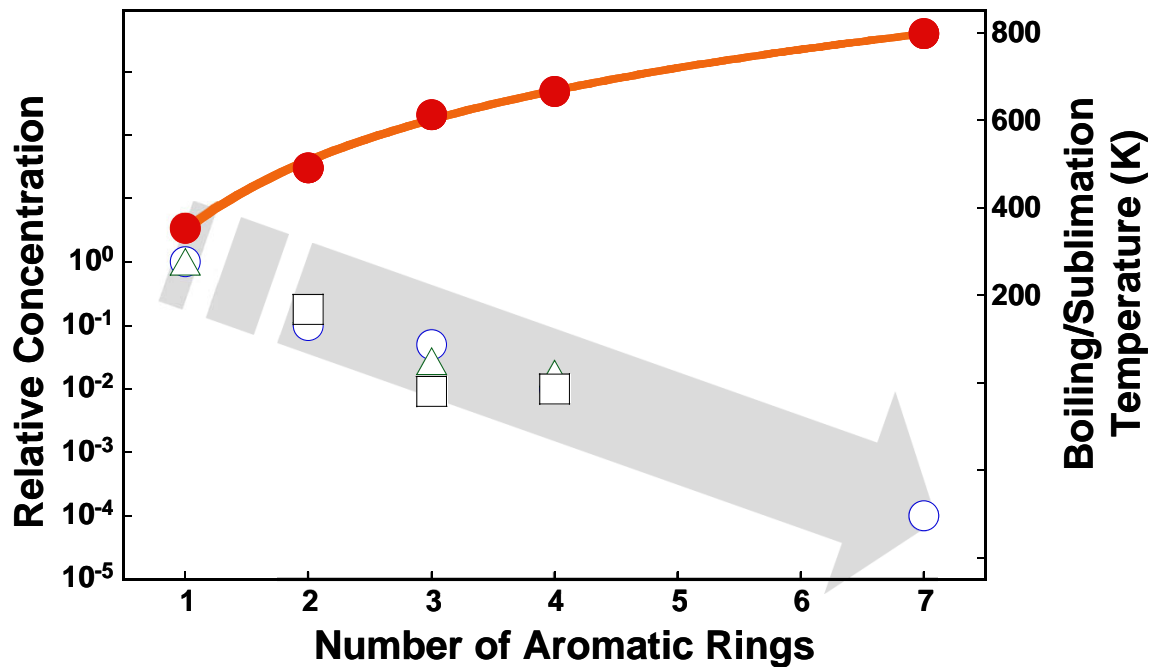


Soot Nucleation (2)



Herdman and Miller (2008)

Binding energy of coronene = 25 kcal/mol



Soot Nucleation (3)

Is 25.4 kcal/mol enough to bind a pair of coronene together?



$$\Delta H^\circ \cong -E_0 + \sum_{i=1}^6 \left\{ 1 + \frac{1}{\exp[h\nu_i/(k_B T)] - 1} \right\} h\nu_i - 4k_B T$$

$$\frac{\Delta S^\circ}{R_u} \cong \ln \left[\left(\frac{2\bar{B}}{m} \right)^{3/2} \frac{h^3 p^0}{\pi^2 (e k_B T)^4} \frac{\sigma_1^2}{\sigma_2} \right]$$

$$+ \sum_{i=1}^6 \left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln(1 - e^{-h\nu_i/k_B T}) \right]$$

Assumptions:

$$\nu_i = 200 \text{ cm}^{-1}$$

$$B (\text{cm}^{-1}) = 1510 \times MW^{-2.12}$$

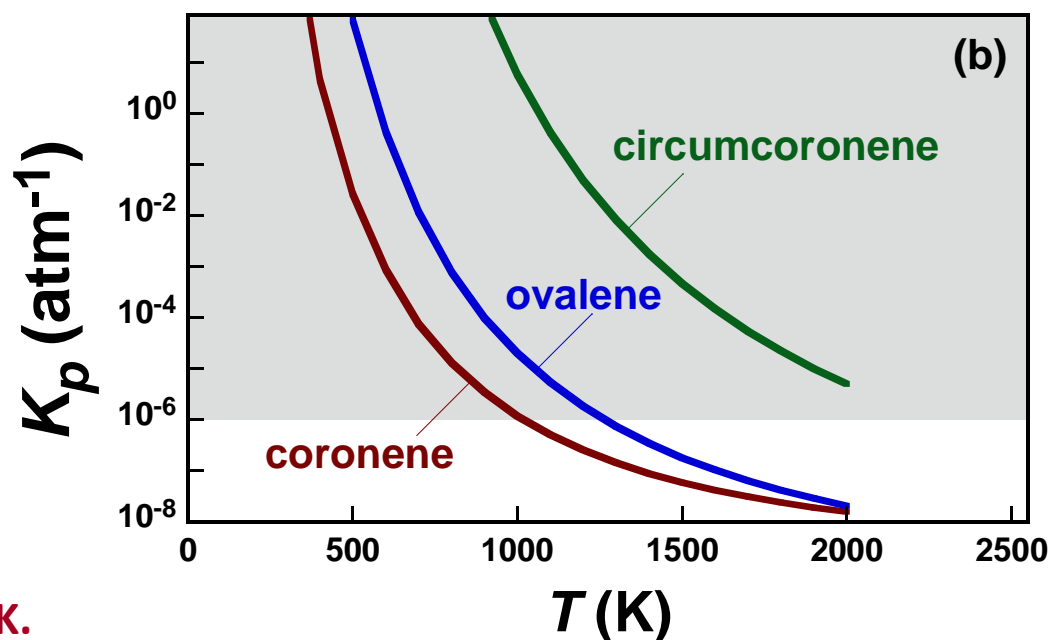
$$\sigma_2 = 1$$

Ovalene $E_0 = 35$ kcal/mol

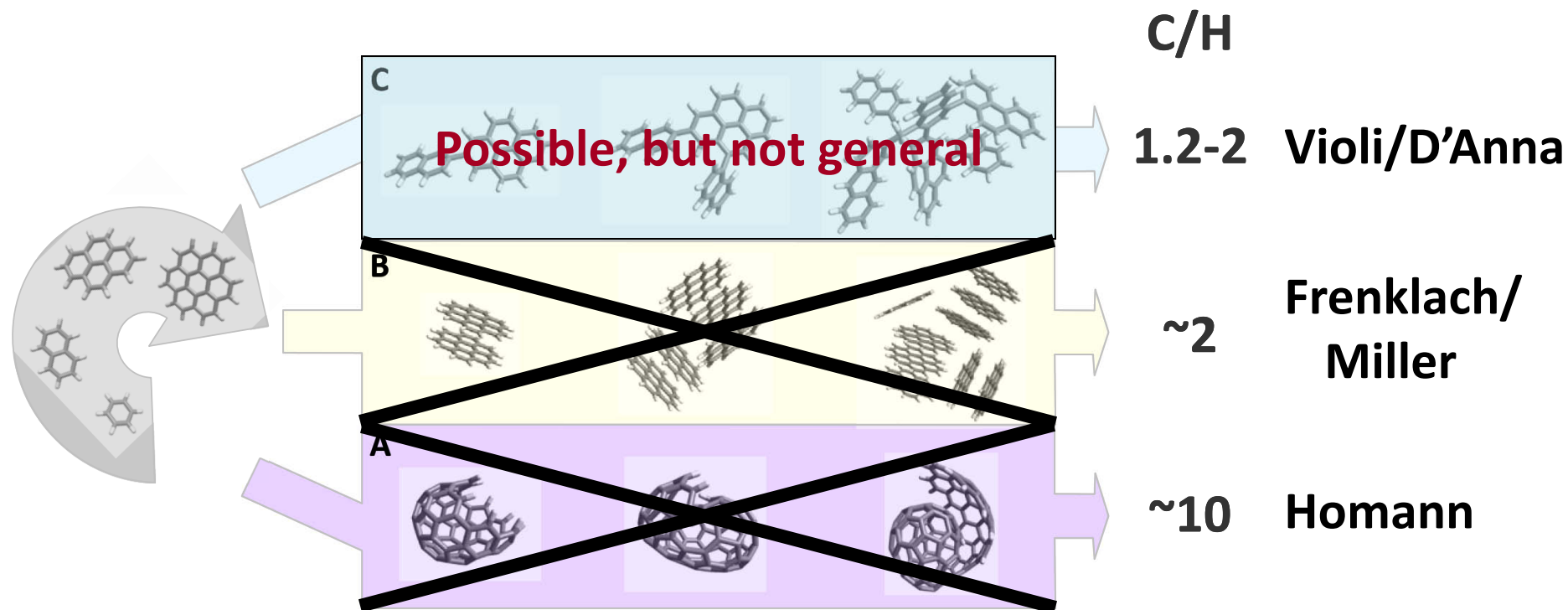
Circumcoronene $E_0 = 63$ kcal/mol

Only circumcoronenes bind > 1600 K.

- ΔG° too positive to allow binding above 1000 K
- Entropy tears the dimer apart.



Soot Nucleation (1)



Soot Nucleation (4)

- Polyacenes are singlet diradicals (though arguable).
- Ground-state polyacenes are close-shell singlets, but the adiabatic S0-T1 excitation energy is only 13 kcal/mol for heptacene - Hajgató et al. (2009).
- Applications in organic light emitting diodes and organic semiconductors and capacitors.



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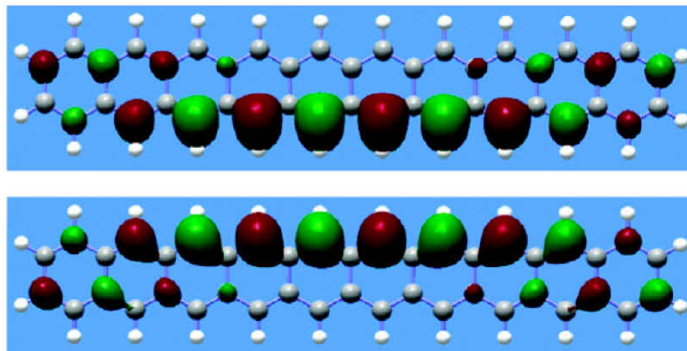
Communication

Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States

Michael Bendikov, Hieu M. Duong, Kyle Starkey, K. N. Houk, Emily A. Carter, and Fred Wudl

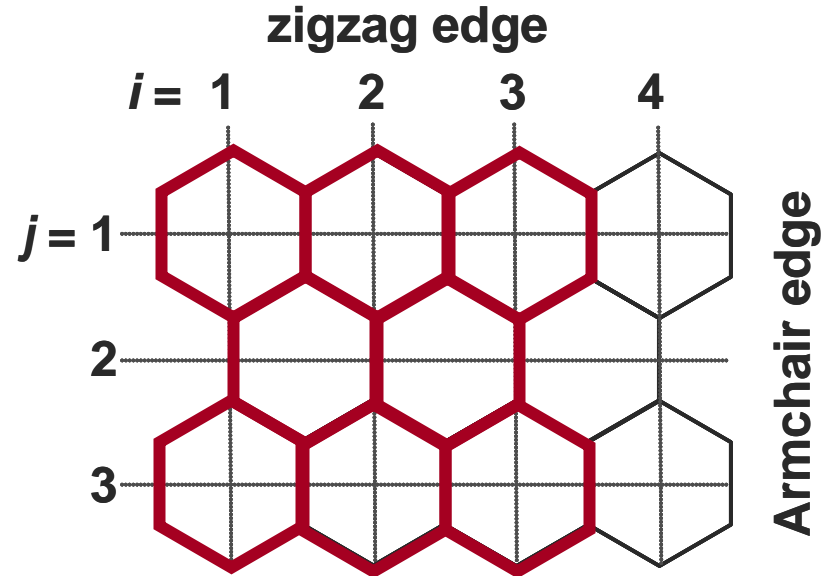
J. Am. Chem. Soc., 2004, 126 (24), 7416-7417 • DOI: 10.1021/ja048919w • Publication Date (Web): 14 May 2004

Downloaded from <http://pubs.acs.org> on March 31, 2009



Soot Nucleation (5)

- Zigzag edges of graphene have localized π -electronic states
Kobayashi 1993; Klein 1994
- Zigzag edges have an open-shell singlet ground state
e.g., Fujita et al. 1996; Nakada 1996
- Finite-sized graphenes have radical or even multiradical characteristics.
e.g., Nakano et al. 2008, Nagai 2010
- Side chain can induce π -radical characteristics
Nakano et al. 2007
- Nonlinear optics applications.



Soot Nucleation - Summary

- If PAHs with π -radicals do play a role in soot nucleation, we need to
 - Understand the nature and structures of these PAH species,
 - Determine their binding energies with relevant species, including aromatics,
 - Probe them in flames (however small their concentrations may be),
 - Account for the mechanism of their formation.

Work Summary

- Products of benzene + O(³P) reaction
- Kinetic modeling studies of iso-butane and iso-butene combustion
- Sooting behaviors of isobutanol and *n*-butanol flames
- Aromatic π -diradicals in soot nucleation and mass growth