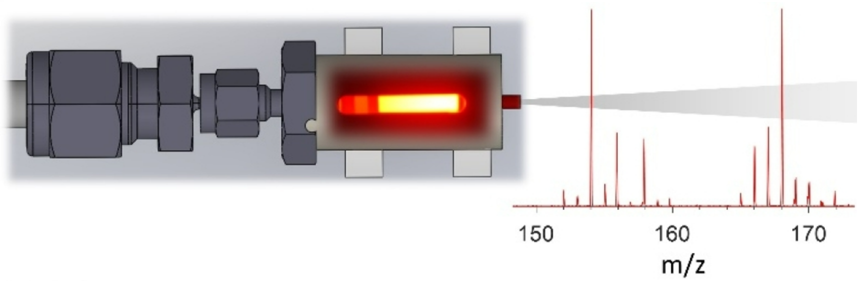
SAND2022-3211C

CHEMISTRY, COMBUSTION, AND MATERIALS CENTER 8300

Gas phase radical-radical chain reactions: Hydrocarbon growth without requiring reactivation



David Couch, Angie Zhang, Goutham Kukkadapu, Craig Taatjes, Nils Hansen

Sandia National Laboratories

March 21, 2022

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Hydrocarbon growth: blessing and curse

Helpful

- Carbon nanotubes
  - Drug delivery
  - Structural material
- Black carbon
  - Nutrient absorber
  - Rubber reinforcement
- Plastics

Harmful

Soot, particulate matter

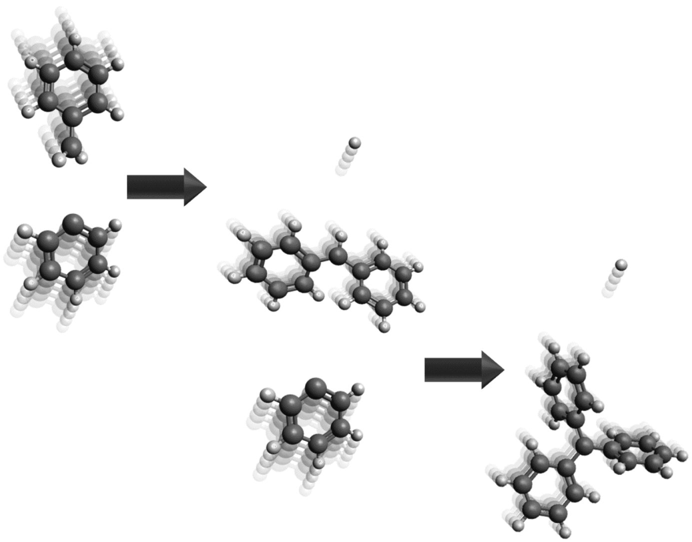
- Sources
  - Wildfires
  - Diesel engines
  - Marine engines
- Effects
  - Respiratory ailment
  - Lung cancer
  - Climate forcing

Interesting

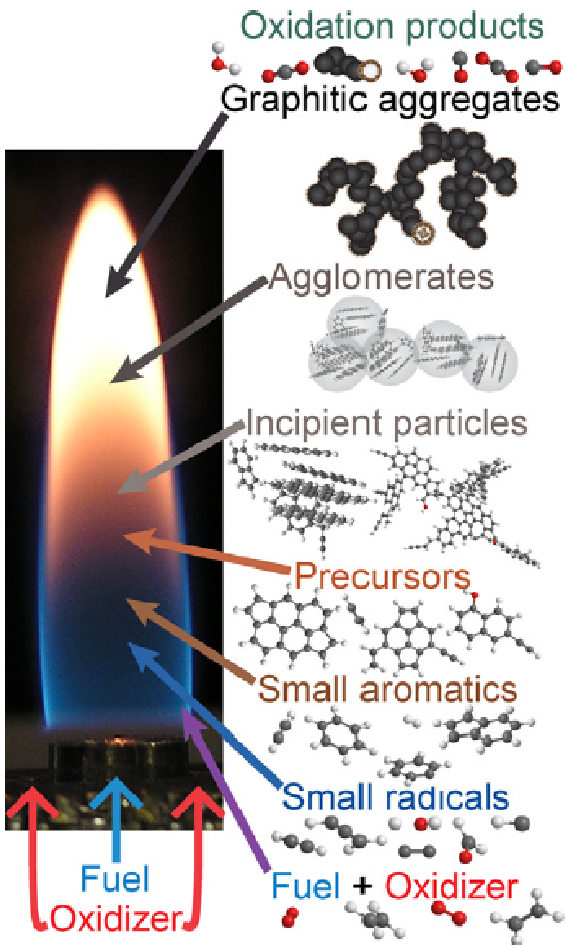
- Polyaromatics in space
  - Likely growing in cold environments

Overview

- "Well-skipping" radical-radical reactions provide a direct chemical pathway from small hydrocarbons to soot inception
- Our result: these reactions are important to soot formation only well below atmospheric pressure
  - Relevant to astrochemistry
  - Likely not relevant in forest fires
  - Not relevant in combustion engines
  - Could be industrially relevant



How does soot form?



Proc. Comb. Inst. ***2017,*** *36, 717-735*

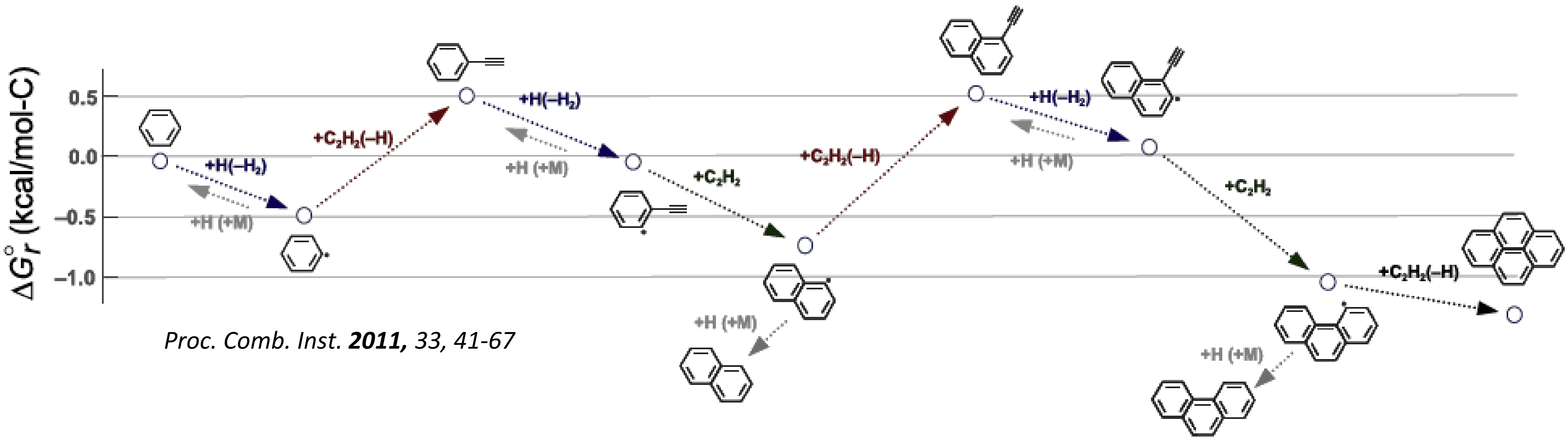
Sticky PAHs

Poly-aromatic hydrocarbons (PAHs)

Aromatic radicals

How does soot form? Adding more rings

- Leading explanation: HACA (Hydrogen abstraction, C_2H_2 addition)



Proc. Comb. Inst. ***2011,*** *33, 41-67*

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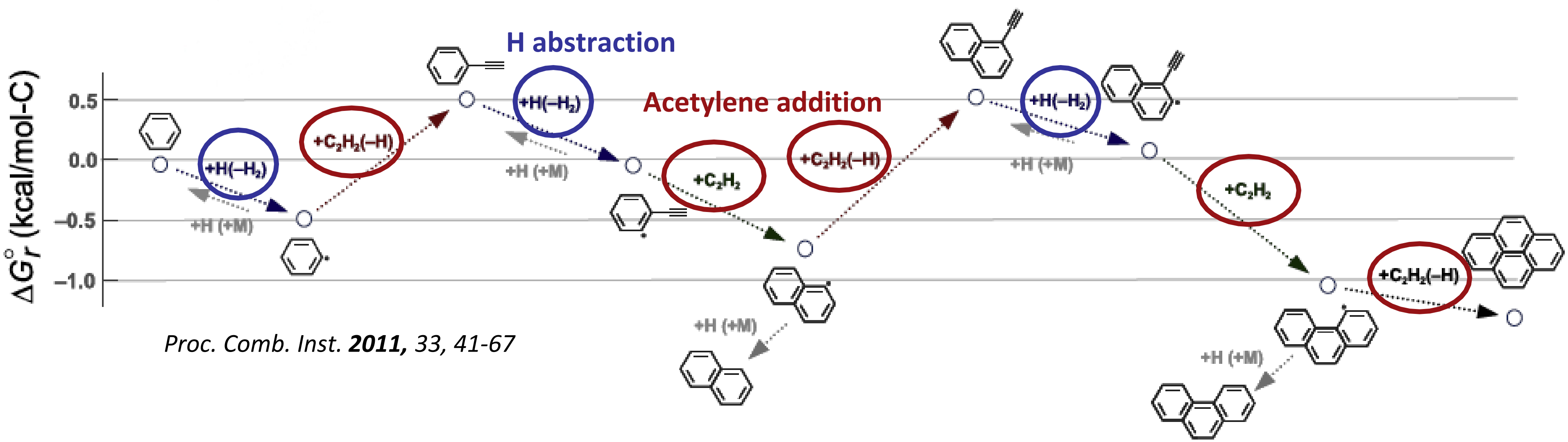

Proc. Comb. Inst. ***2011,*** *33, 41-67*

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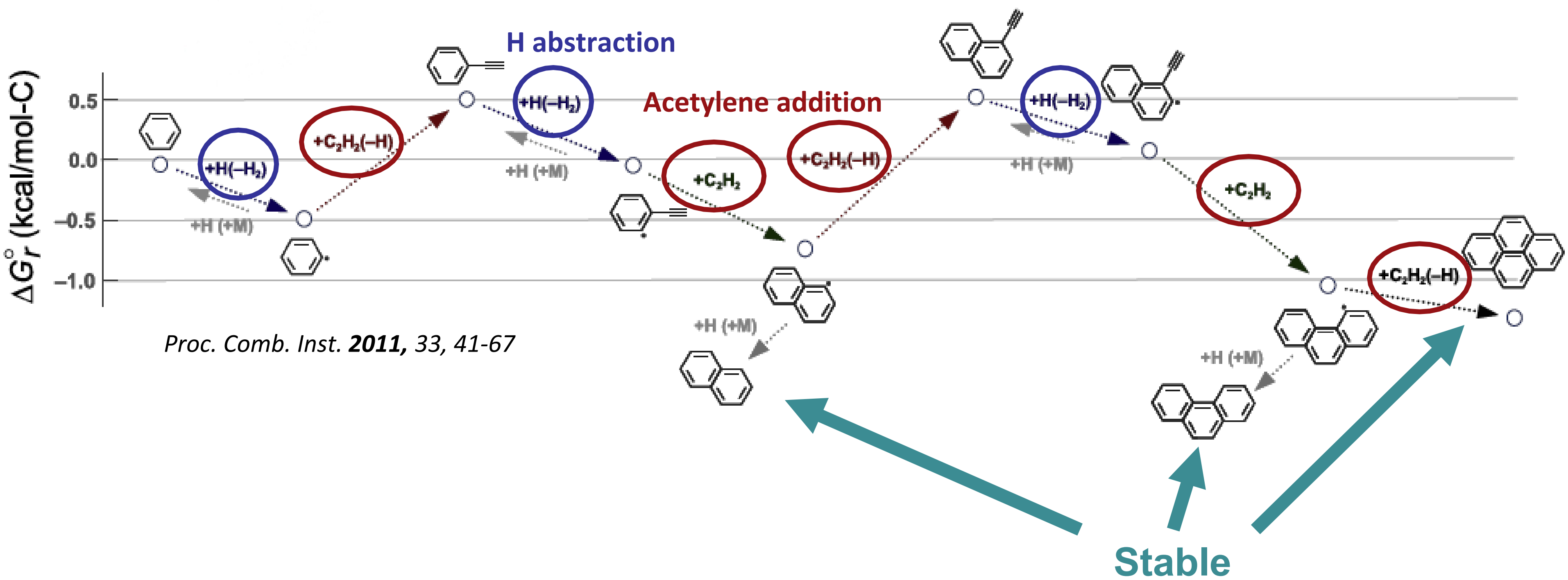

Proc. Comb. Inst. ***2011,*** *33, 41-67*

How does soot form? Adding more rings

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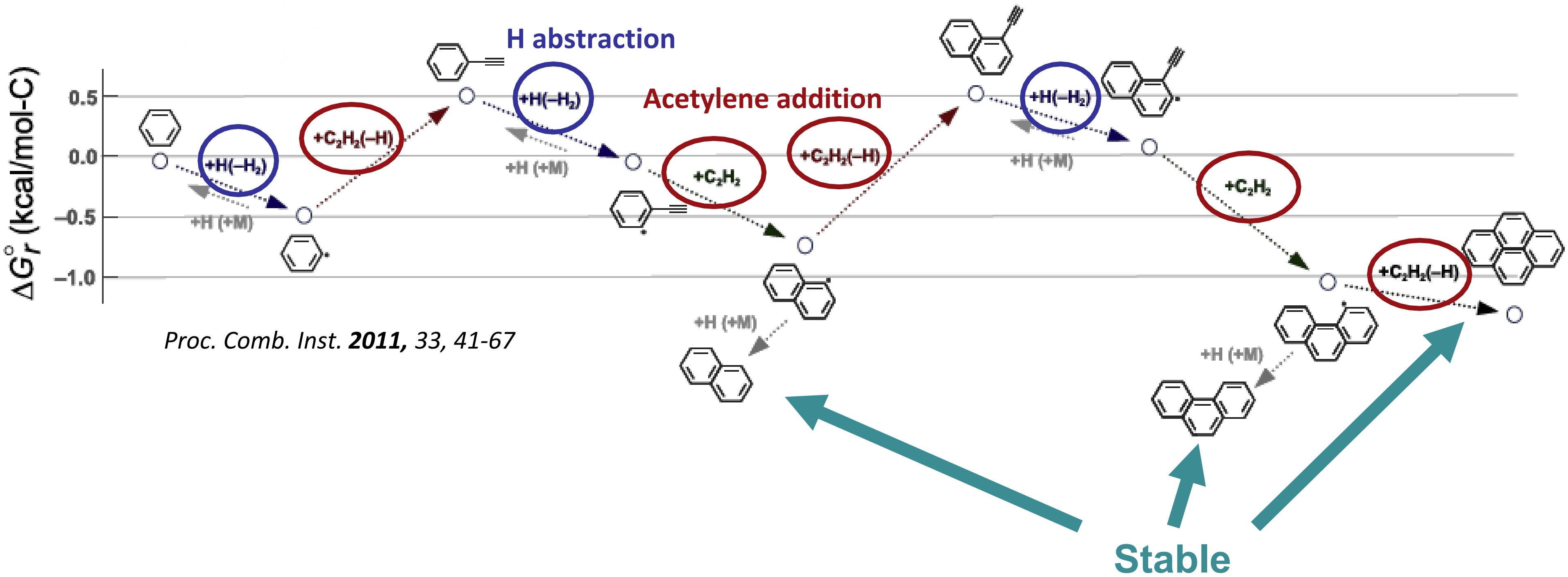
  - Too slow to explain soot
  - Not enough large, stable molecules are observed for this explanation



Proc. Comb. Inst. ***2011,*** *33, 41-67*

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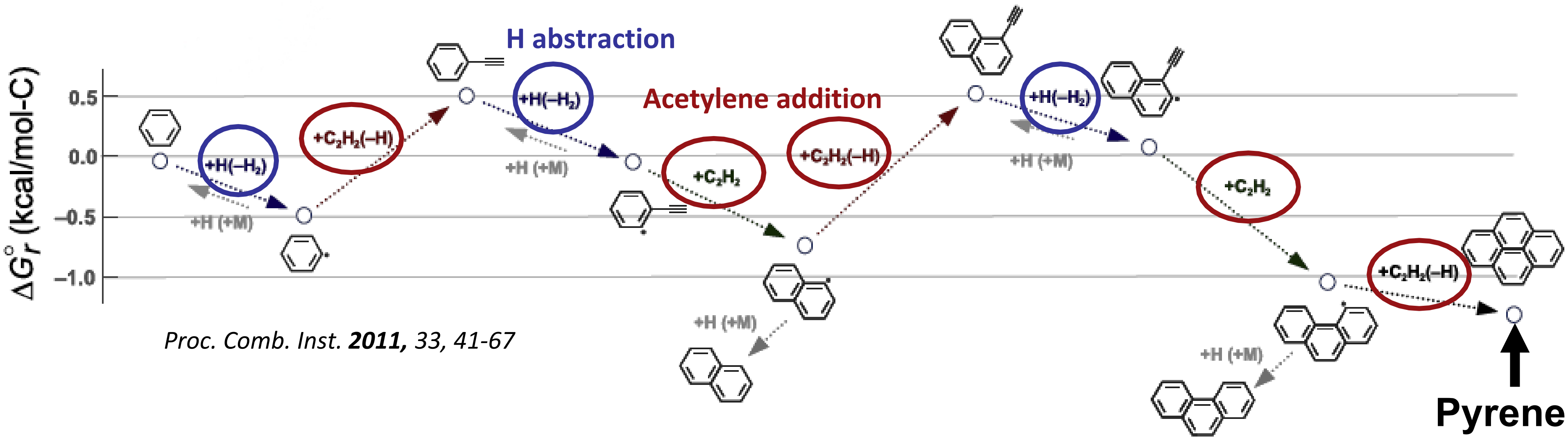
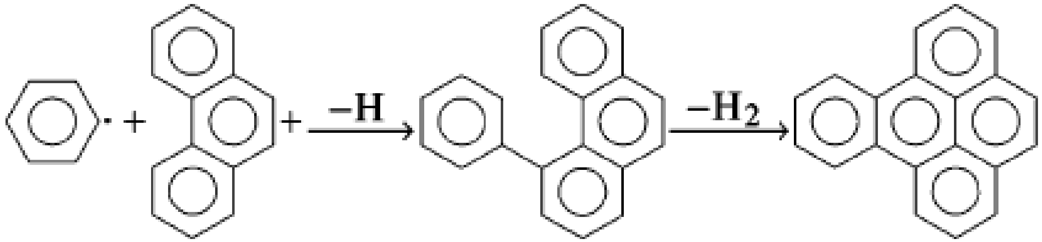


Proc. Comb. Inst. ***2011,*** *33, 41-67*

- Original idea: pyrene can dimerize and make a particle
  - Debunked! A PAH needs around 10-20 rings to dimerize (at 1500 K)!

How does soot form?
Bonds between PAHs

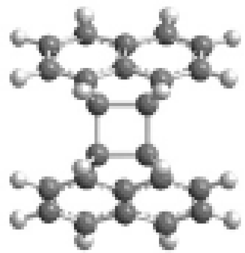
PAC (Phenyl Addition dehydroCyclization)



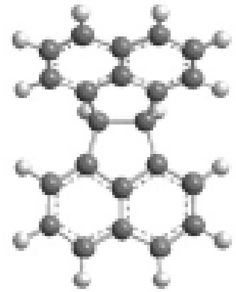
(R3)

JPCA ***2008,*** *112, 2362-2369*

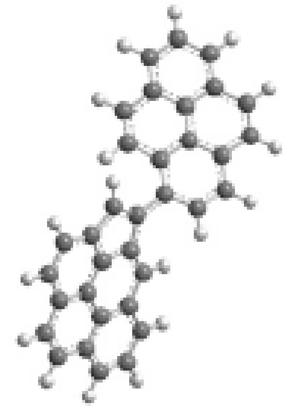
How does soot form? Bonds between PAHs



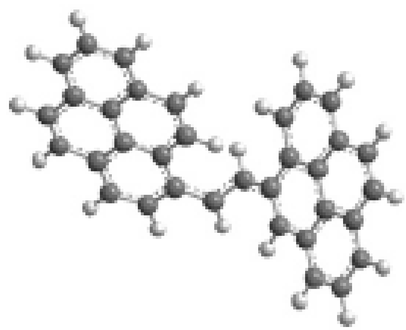
4-center bridge connecting two acenaphthalenes



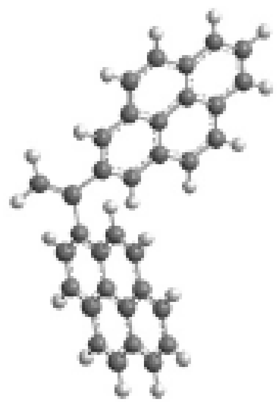
E-bridge connecting two naphthalenes



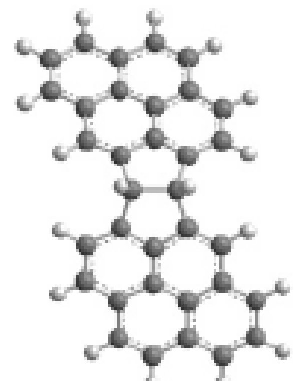
C-C covalent bond bridge



1,2-ethylene bridge



1,1-ethylene bridge

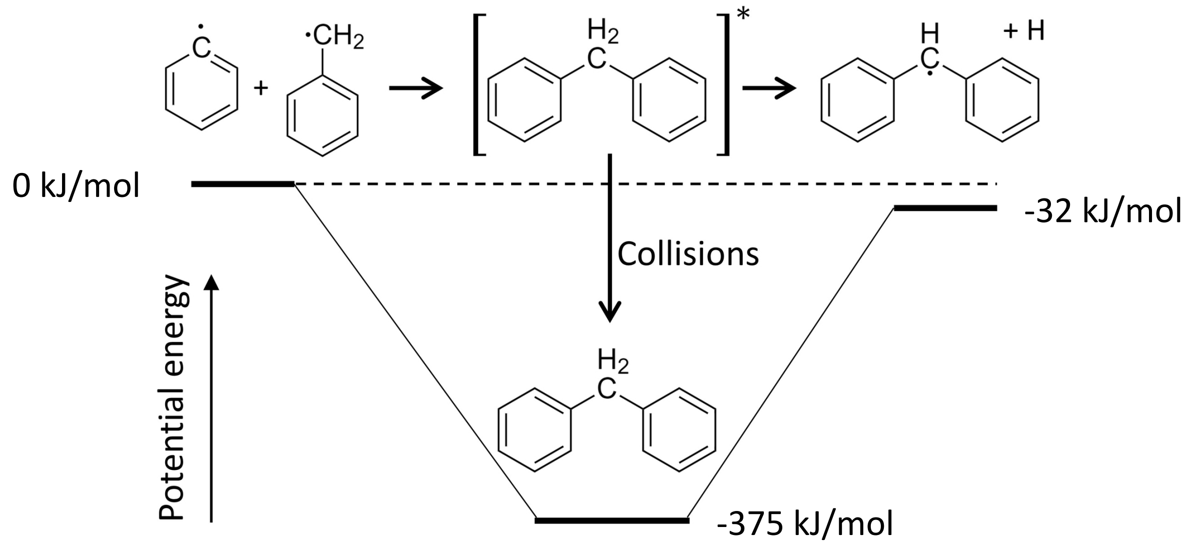


E-bridge connecting two pyrenes

PCCP ***2020***, *22, 5314-5331*

"Well-skipping" non-Boltzmann reactions

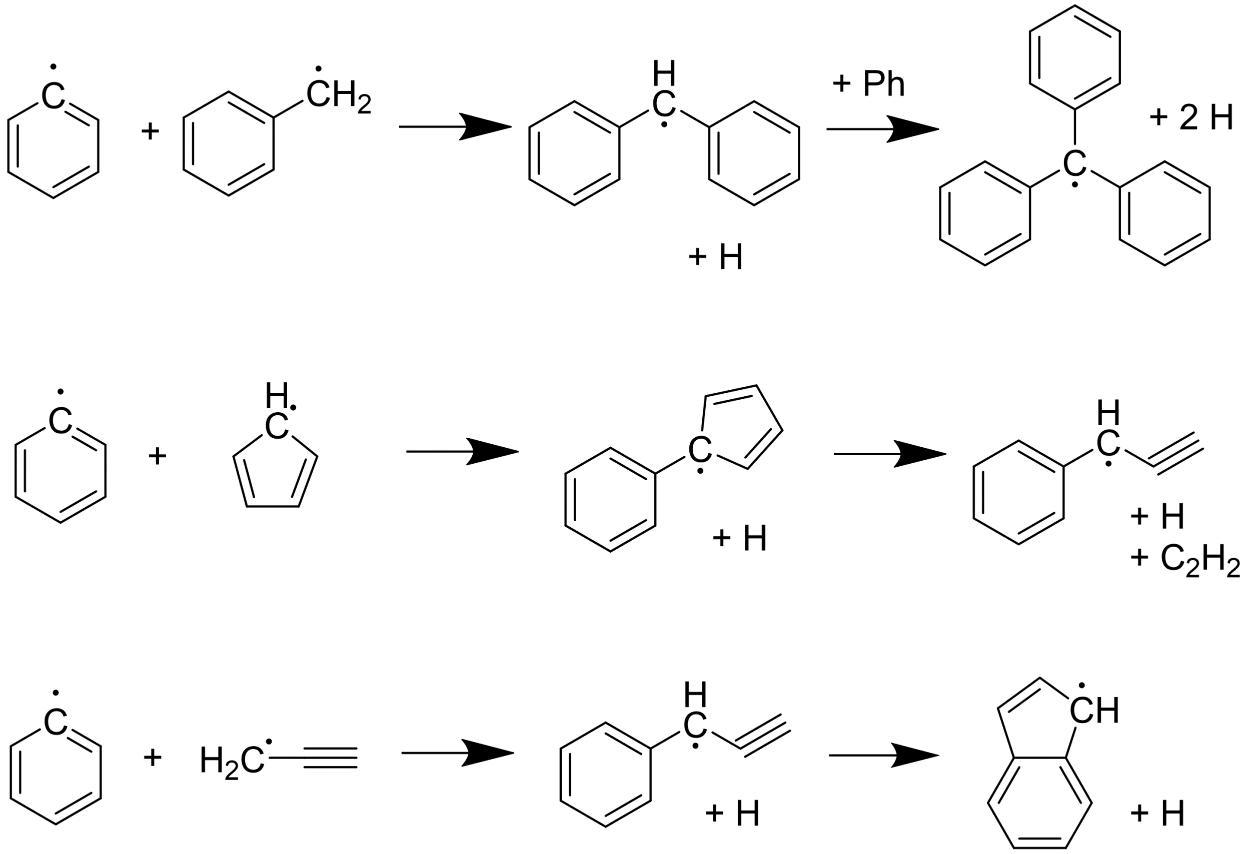
$$Radical + Radical \rightarrow [Adduct]^* \rightarrow Radical + Radical$$



$k_B T \approx 12.5$ kJ/mol (1500 K)

- Radical-propagating
- Reactivation only required when caught in the "well"
- Rate depends on temperature and pressure

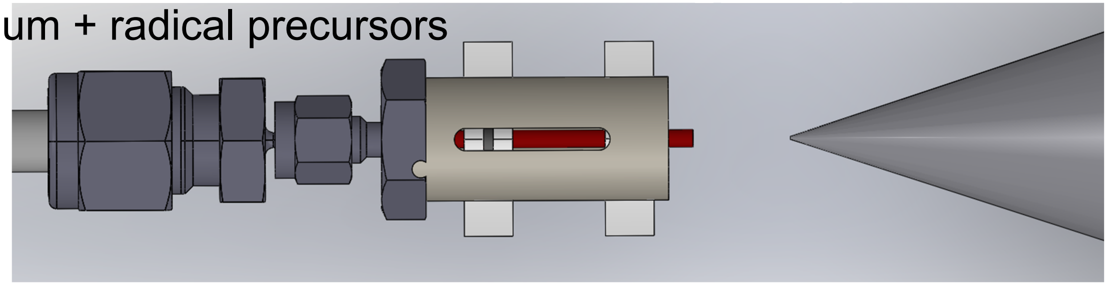
3 Well-skipping reactions that make soot precursors

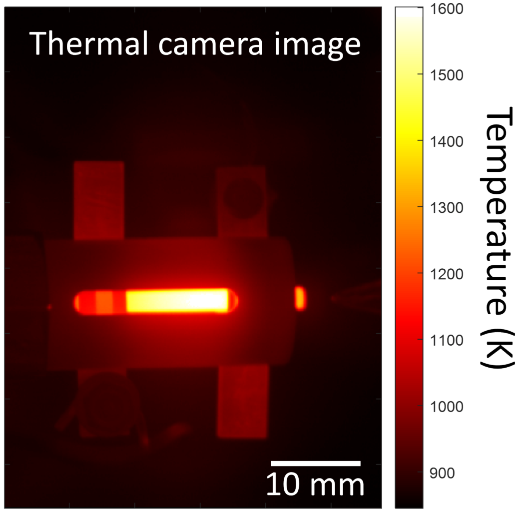


Apparatus

- Flash pyrolysis (~100 μs)

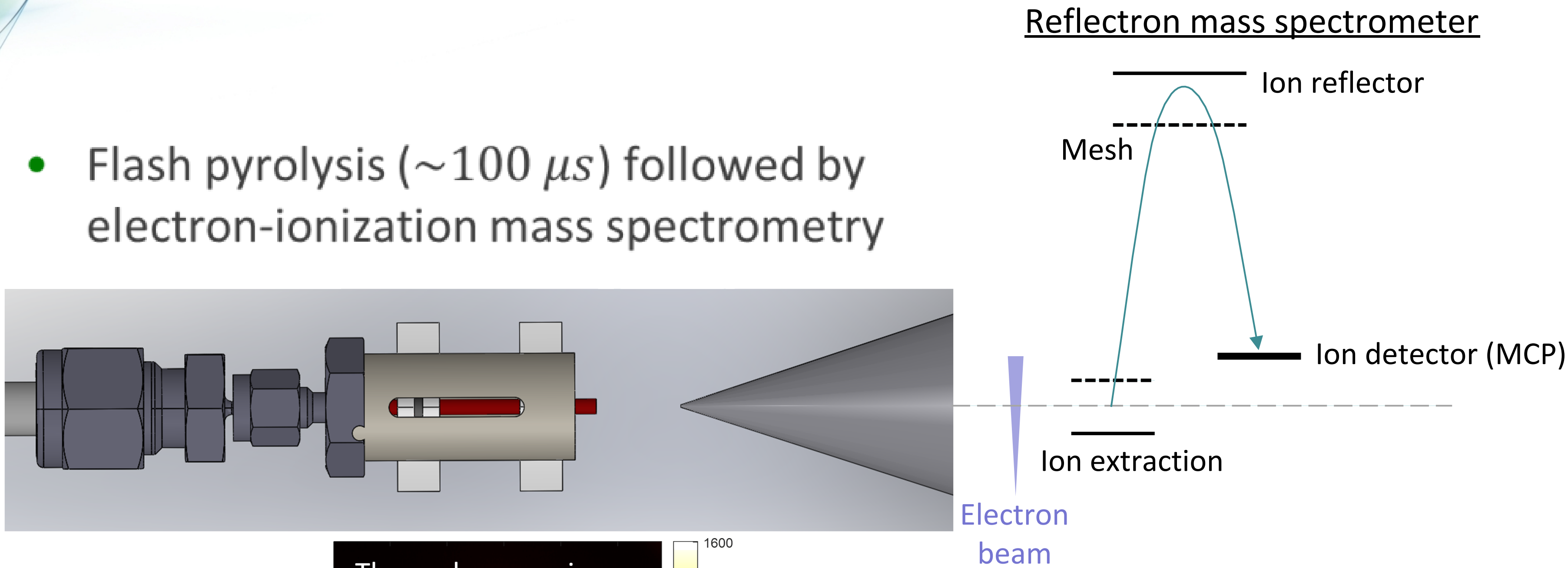
Helium + radical precursors

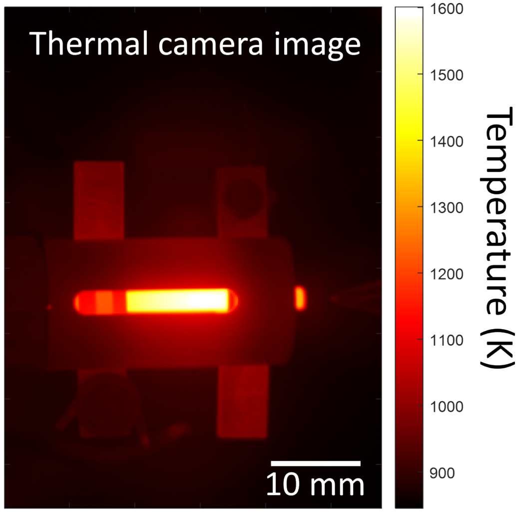




Apparatus

- Flash pyrolysis (~100 μs) followed by electron-ionization mass spectrometry





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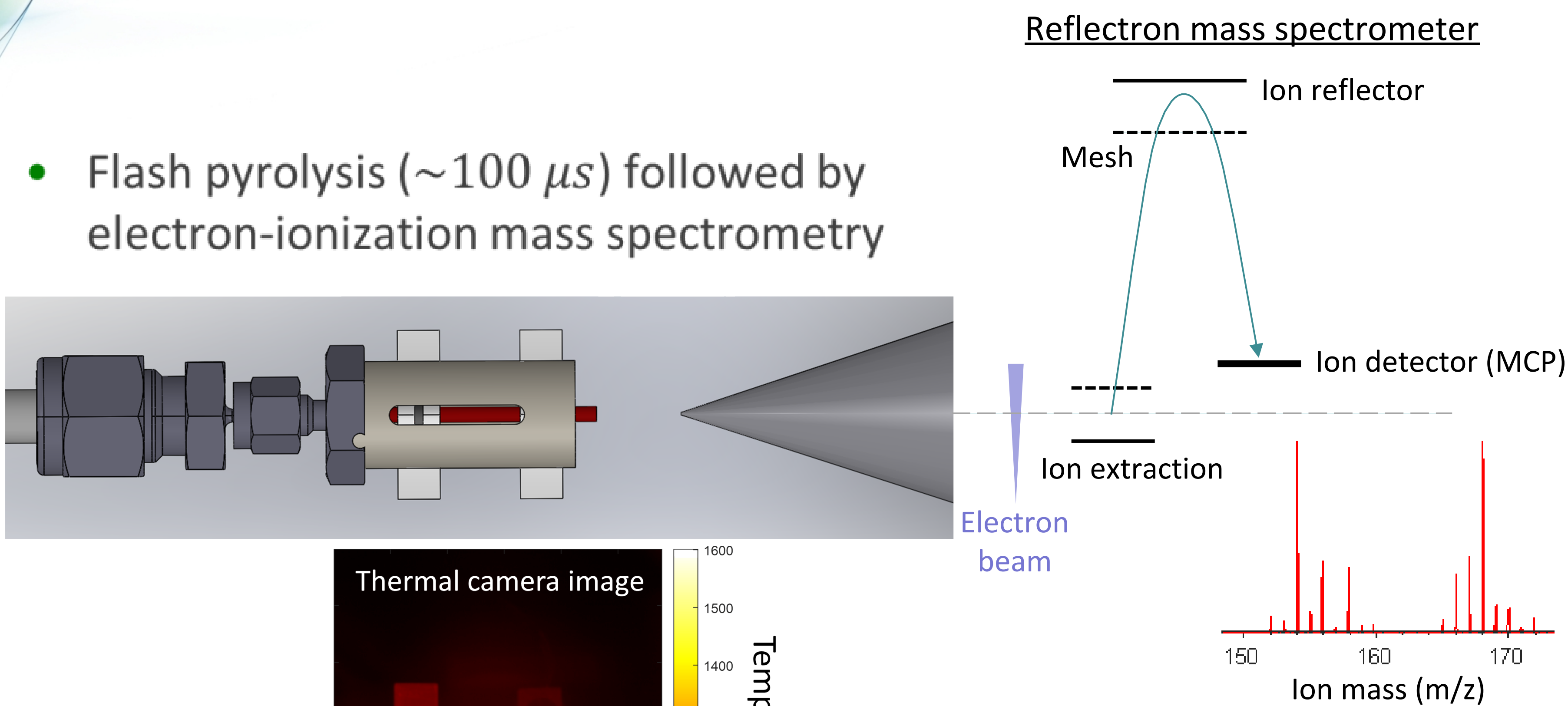

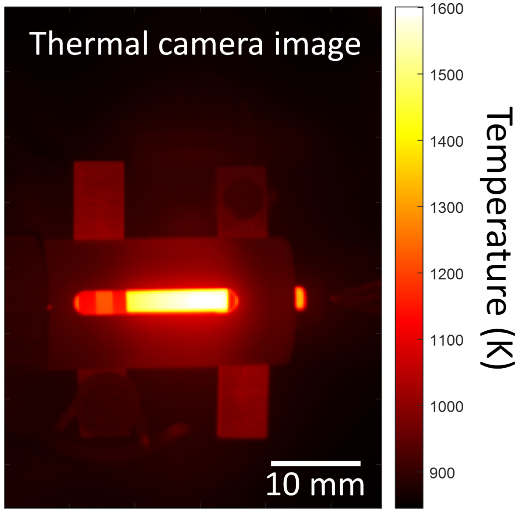

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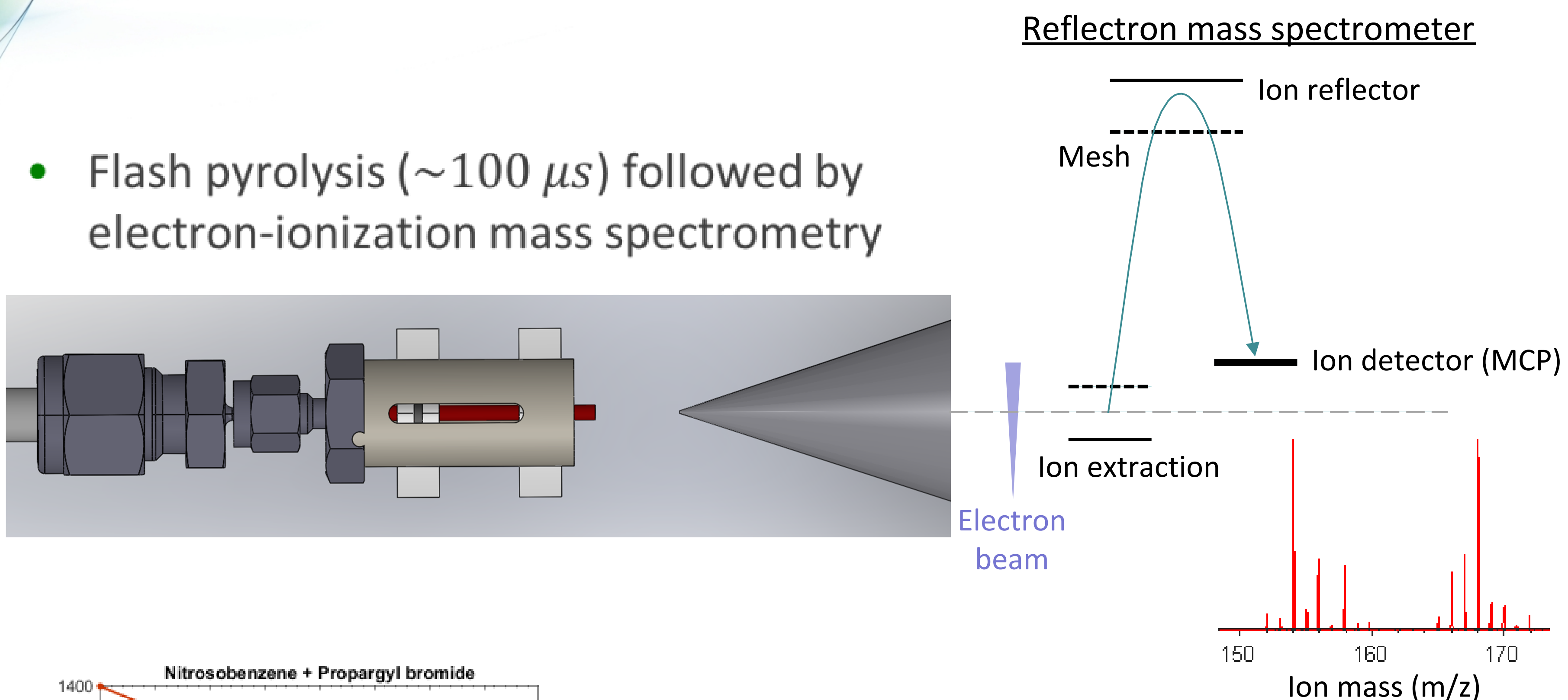
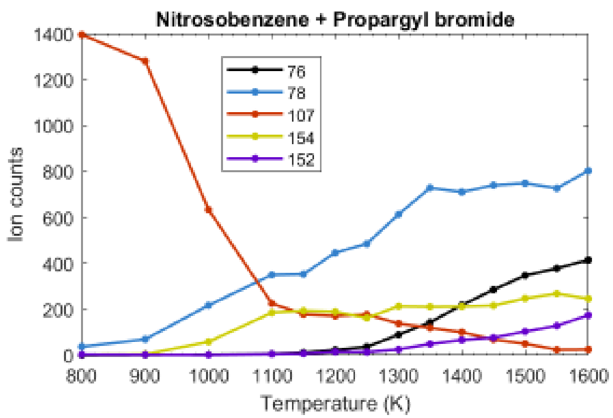
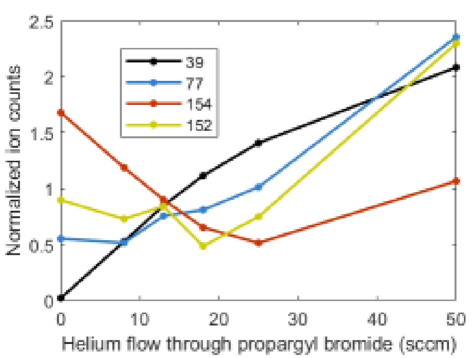
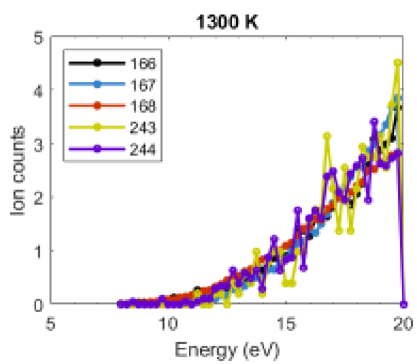




Temperature

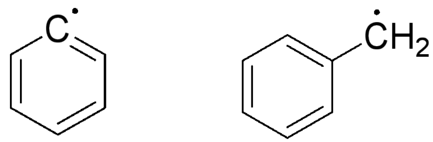


Reactant concentration

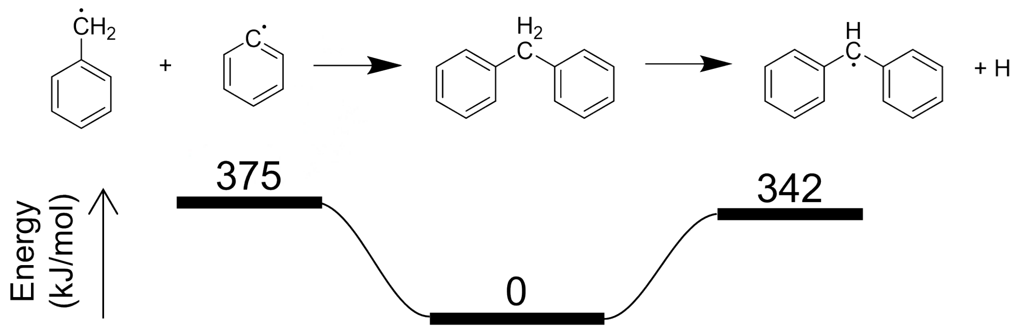


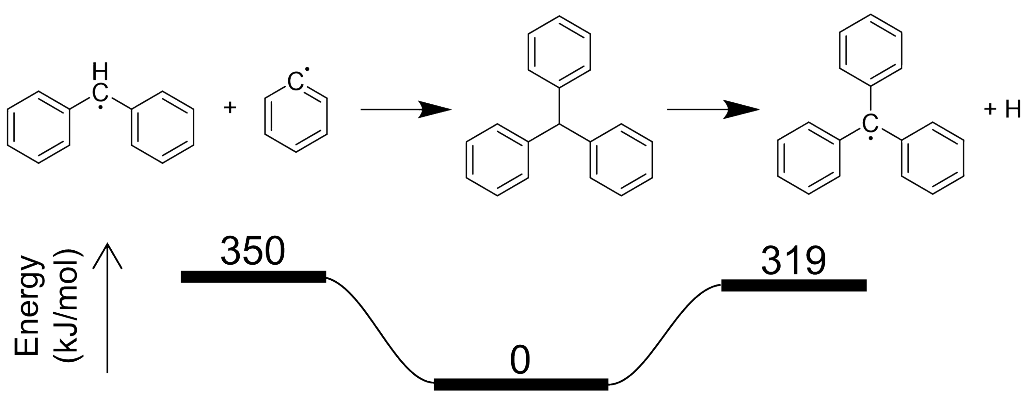
Electron energy

Phenyl + Benzyl



- Chain reaction – the product becomes the reactant





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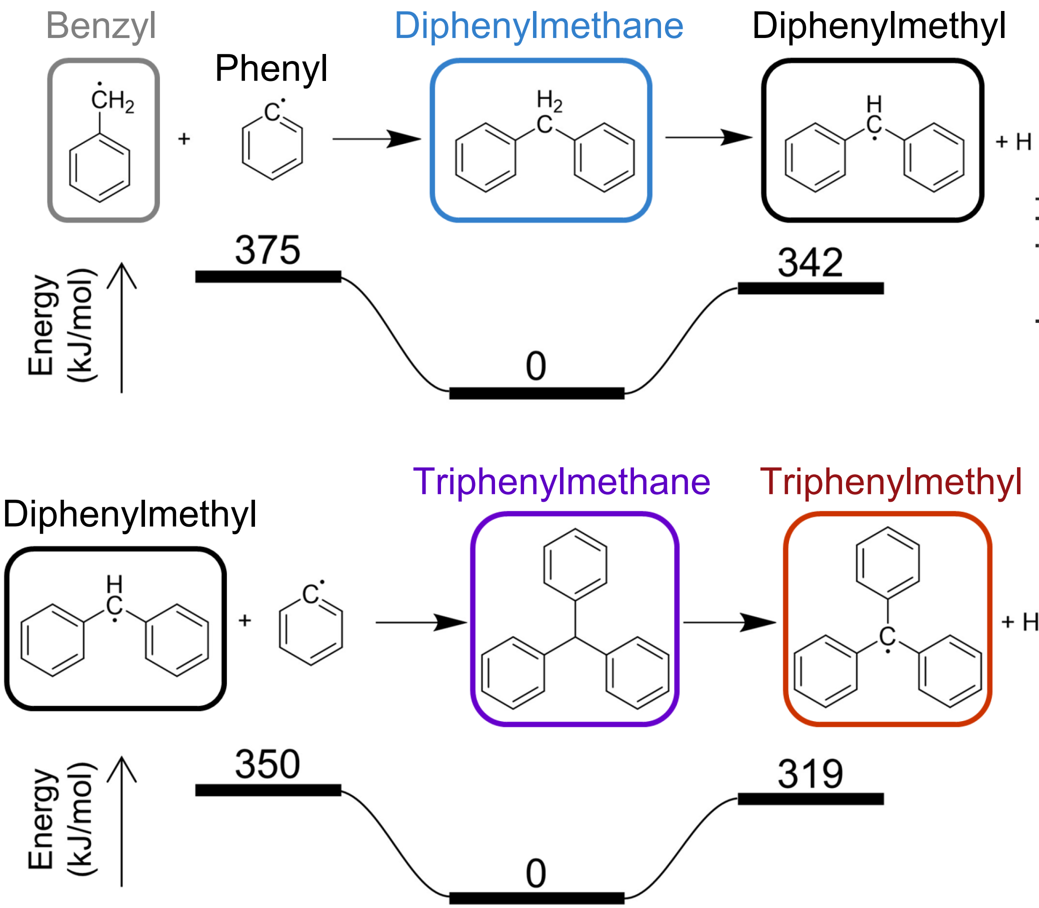
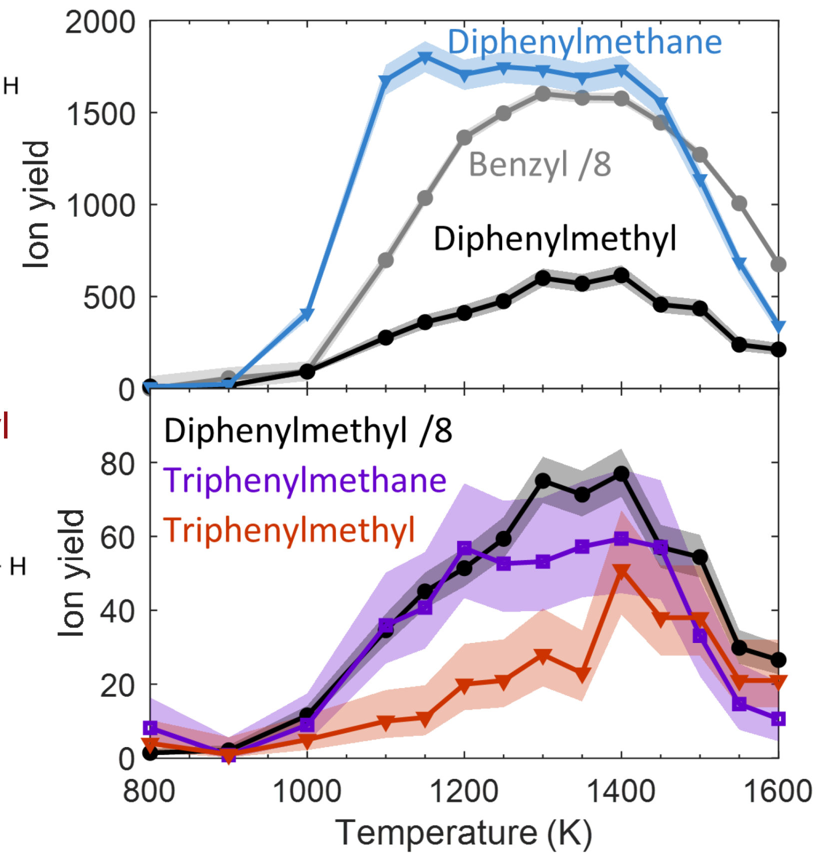
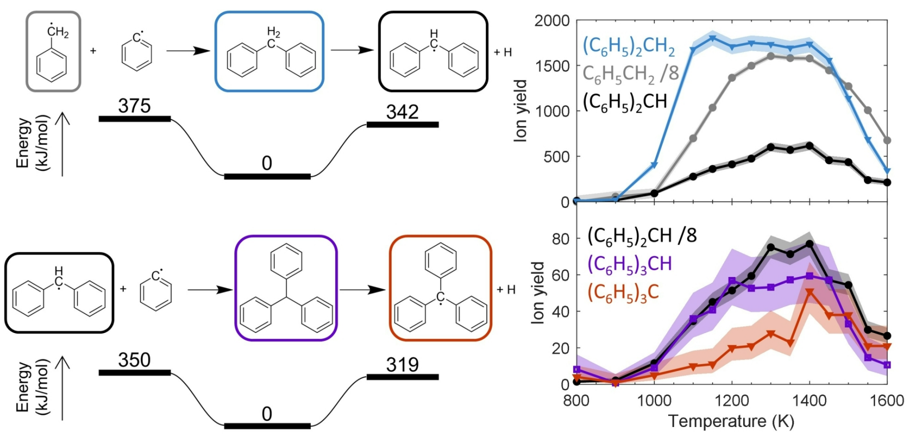
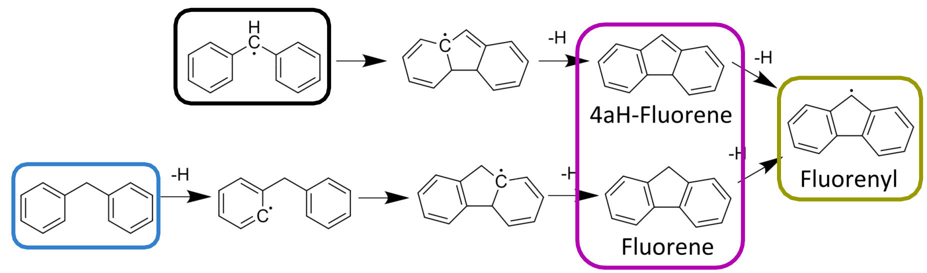


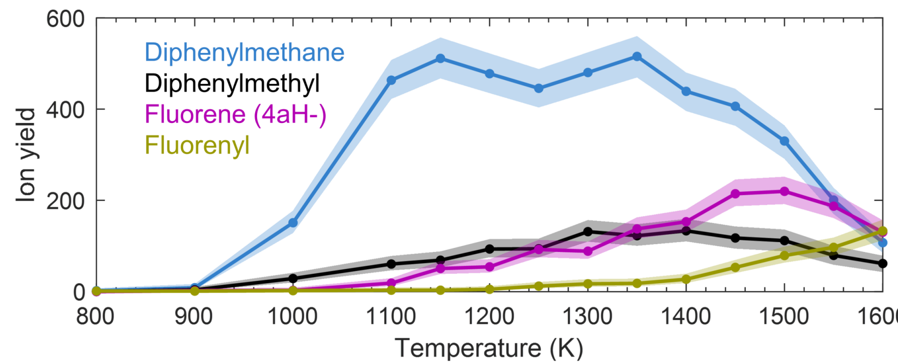


Phenyl + Benzyl

- Chain reaction – the product becomes the reactant
- Decomposition competes with further growth
  - 5-member-ring radicals are quite stable

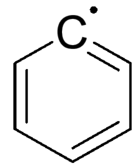






Ange. Chem. Int. Ed. ***2021****, 60, 27230-27235*

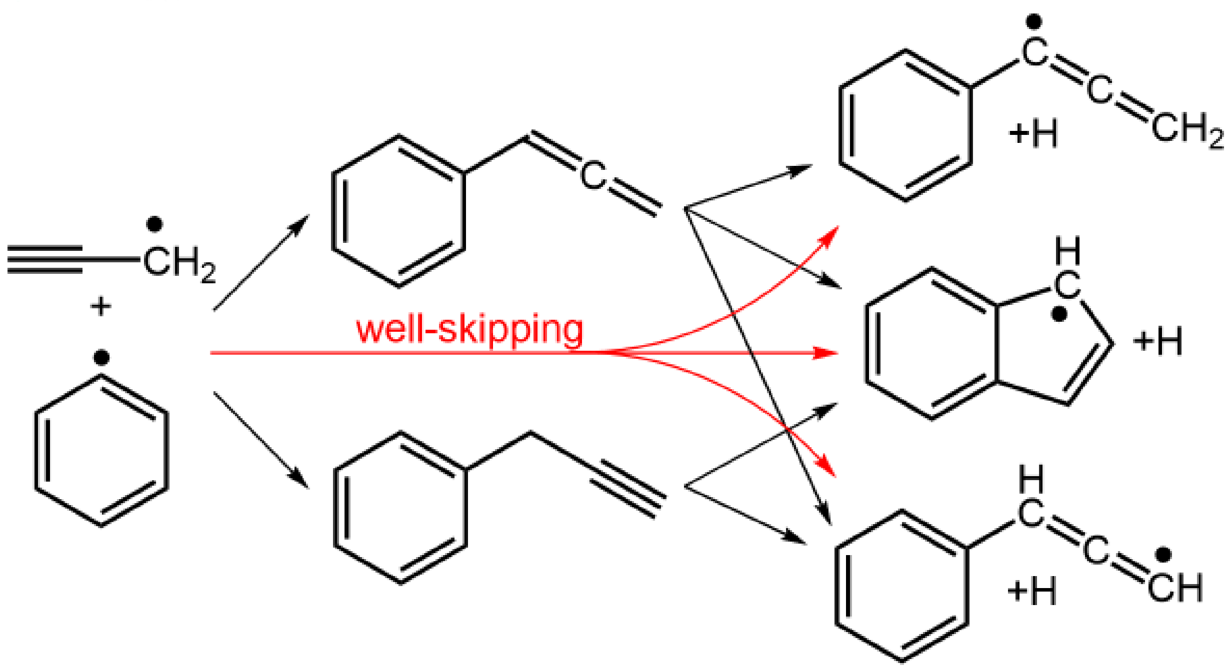
Phenyl + Propargyl



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

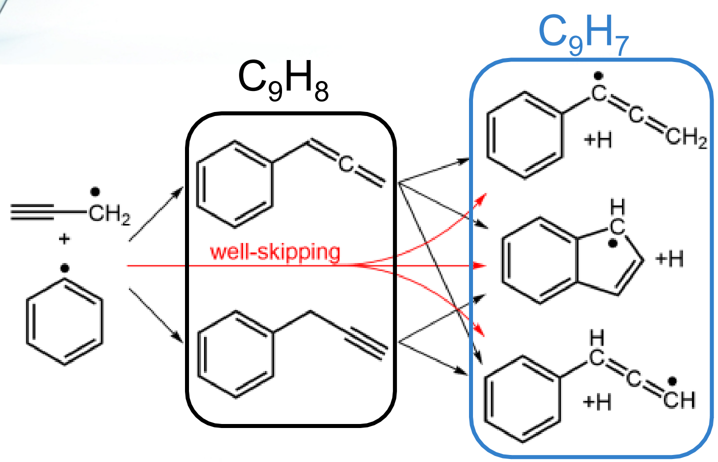
- Both radicals are thermally stable to 1600+ K
- This reaction may resemble other σ-radical + π-radical reactions
- Reaction rates have been calculated by experts

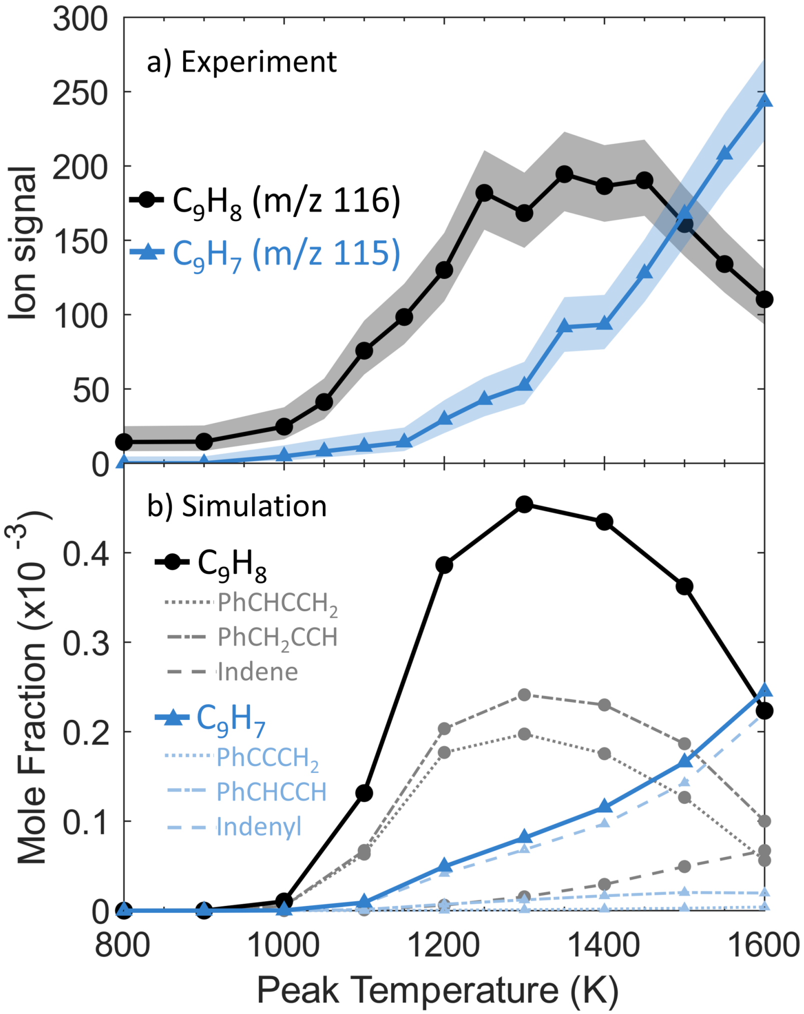
*Rates from PCCP **2020**, 22, 6868-6880*



No further decomposition

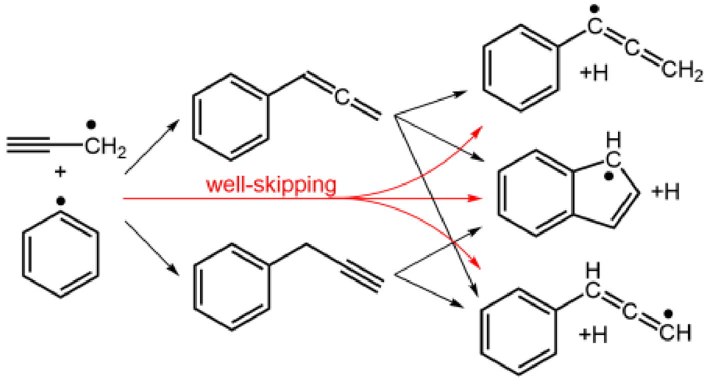
Phenyl + Propargyl



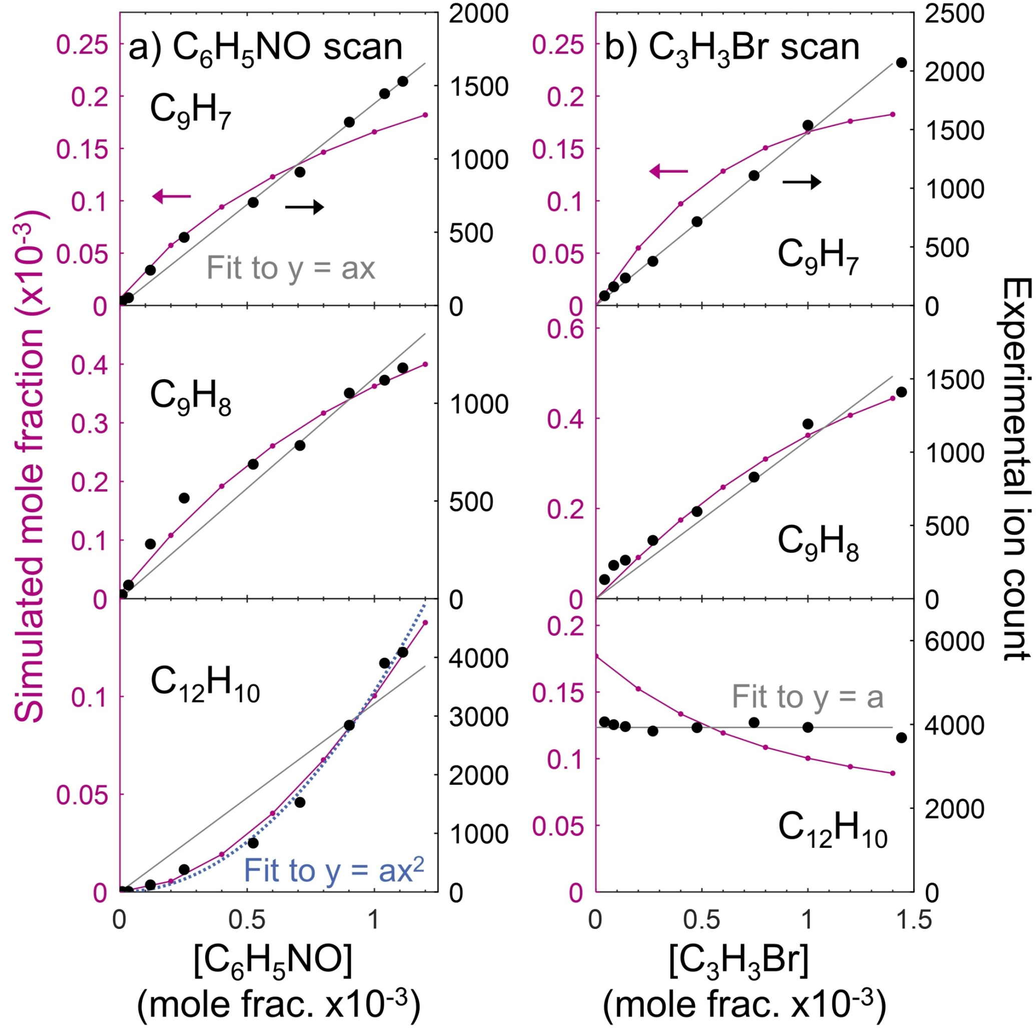


- The experiment cannot distinguish isomers
- The simulation agrees pretty well with experiment
- C_9H_7 is mostly indenyl radical according to simulation

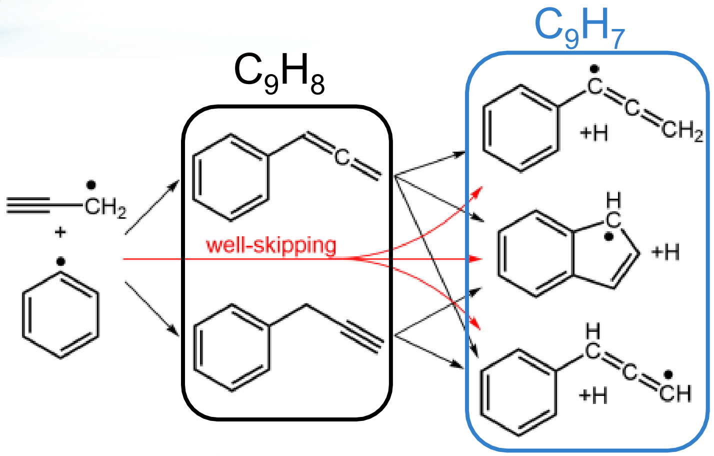
Phenyl + Propargyl

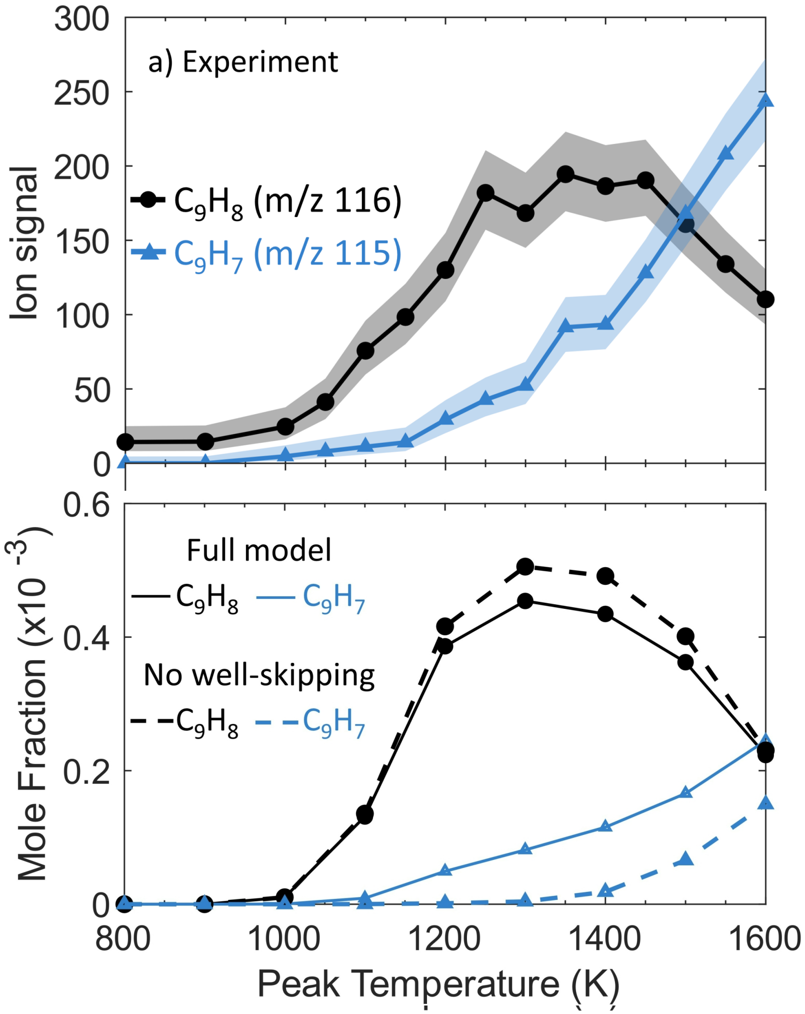


- We scanned each precursor concentration
- Concentration dependence of each species agrees well with the simulation

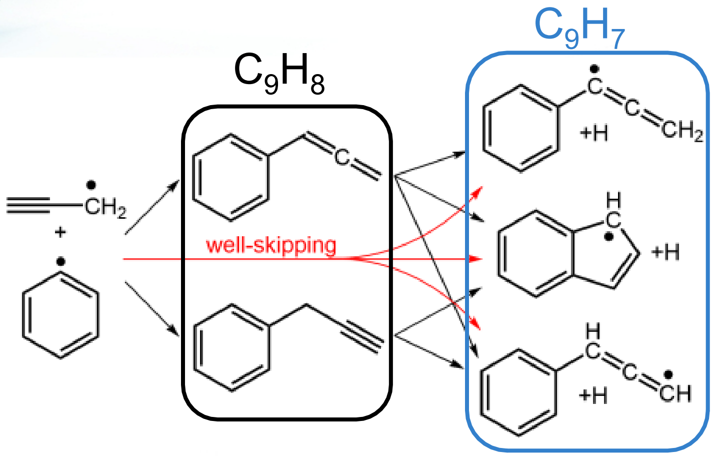


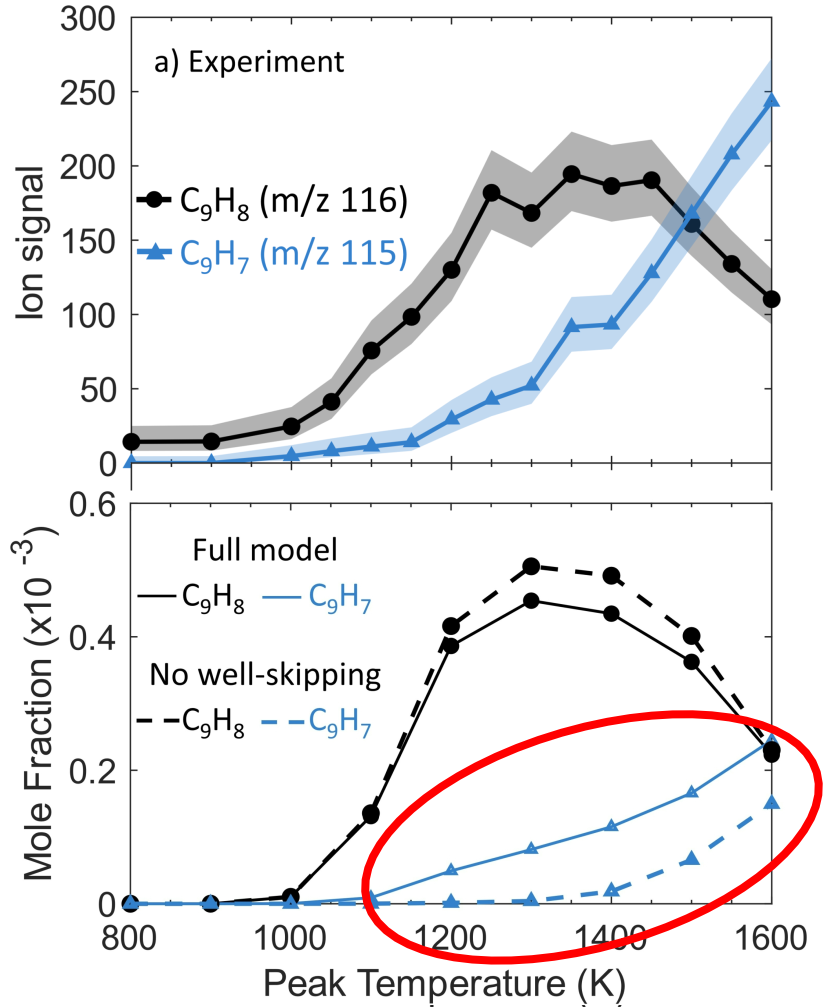
Phenyl + Propargyl





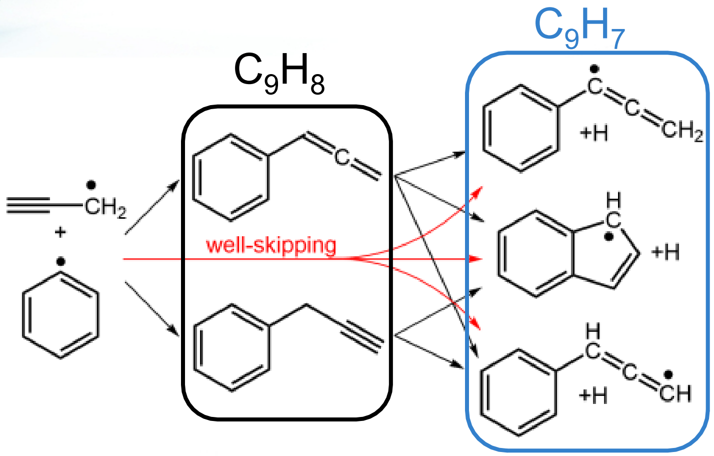
Phenyl + Propargyl



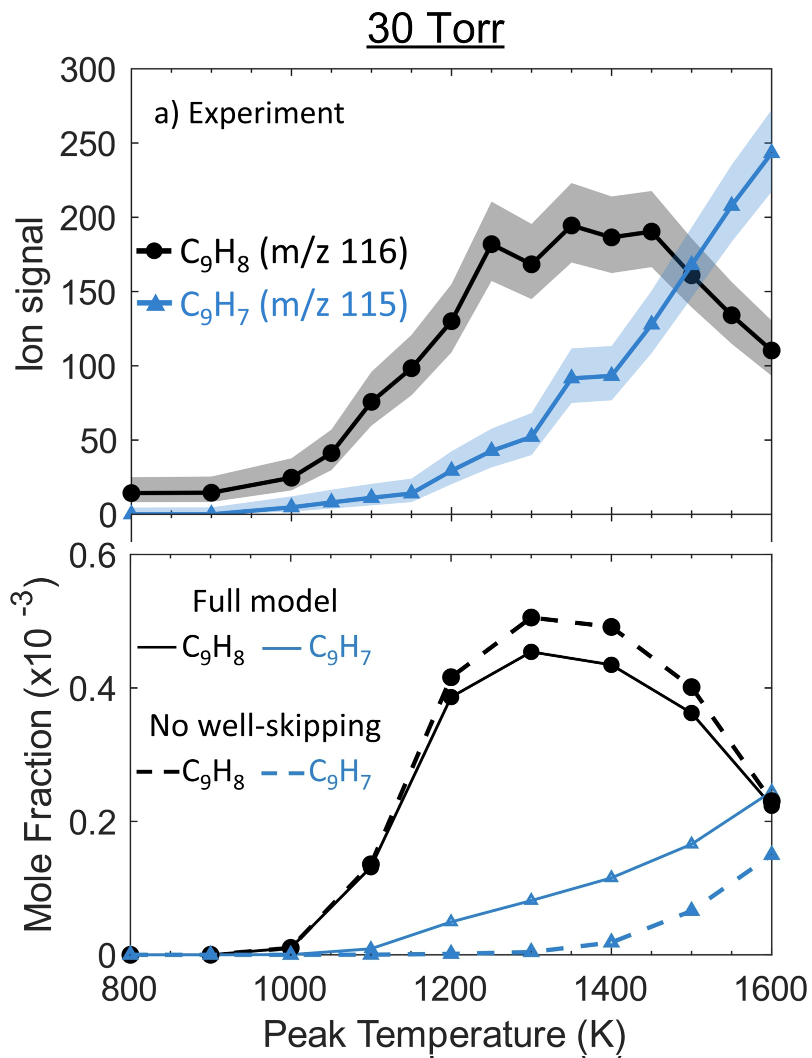


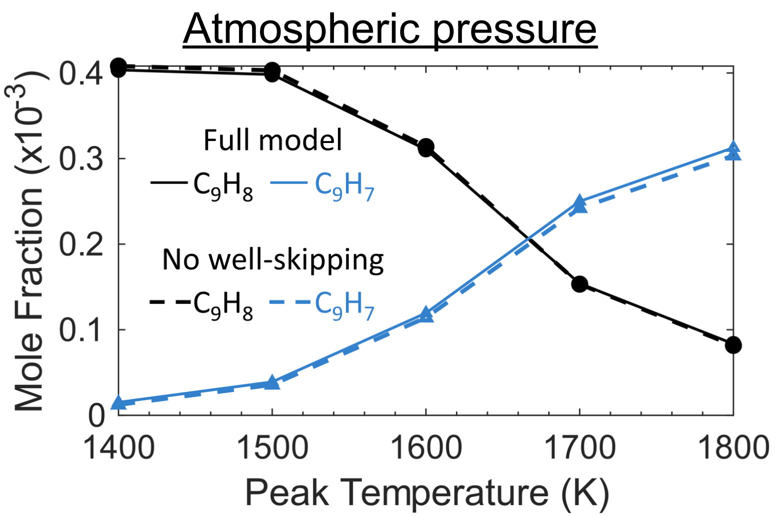
- We cut well-skipping from the simulation
- C_9H_7 yield changes, no longer agrees with experiment
- Conclusion – well-skipping is the dominant source of C_9H_7 here
  - Though C_9H_8 yield is higher

Phenyl + Propargyl

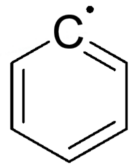


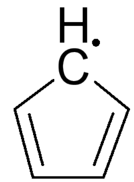
- Well-skipping is negligible at atmospheric pressure





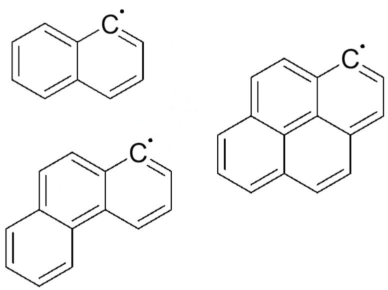
Phenyl + Cyclopentadienyl



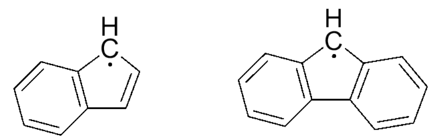


- Simplest in a class of (mostly) unexplored reactions

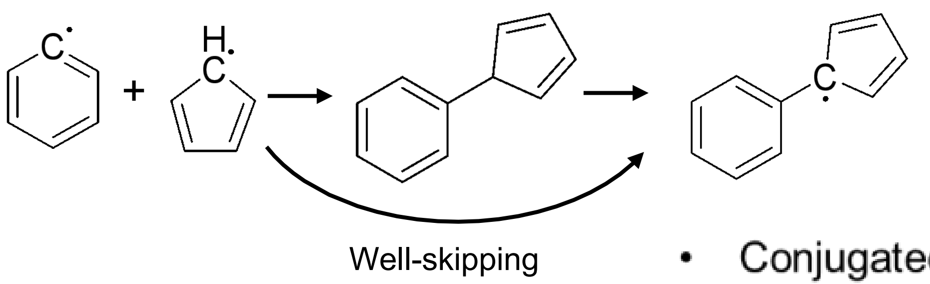
Aryl σ radicals



Resonance-stabilized π radicals

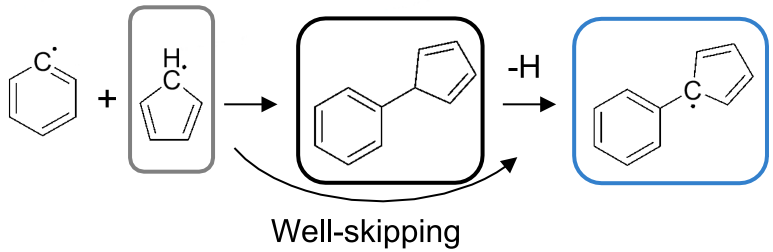


- Great well-skipping candidate

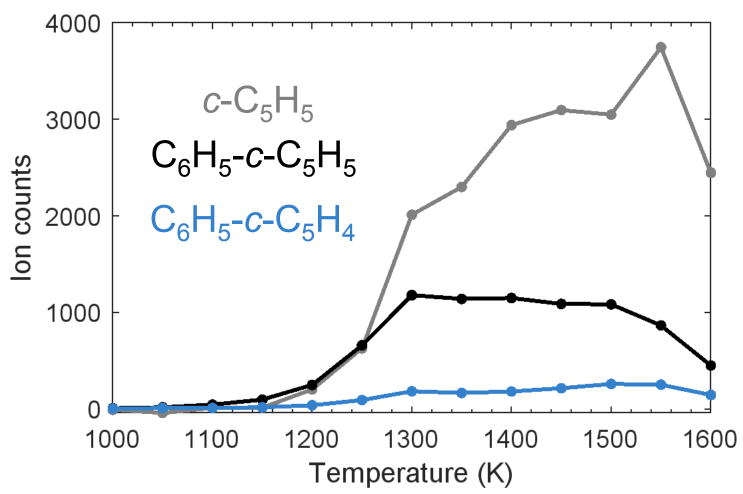


- Conjugated π radical
- No favorable H loss

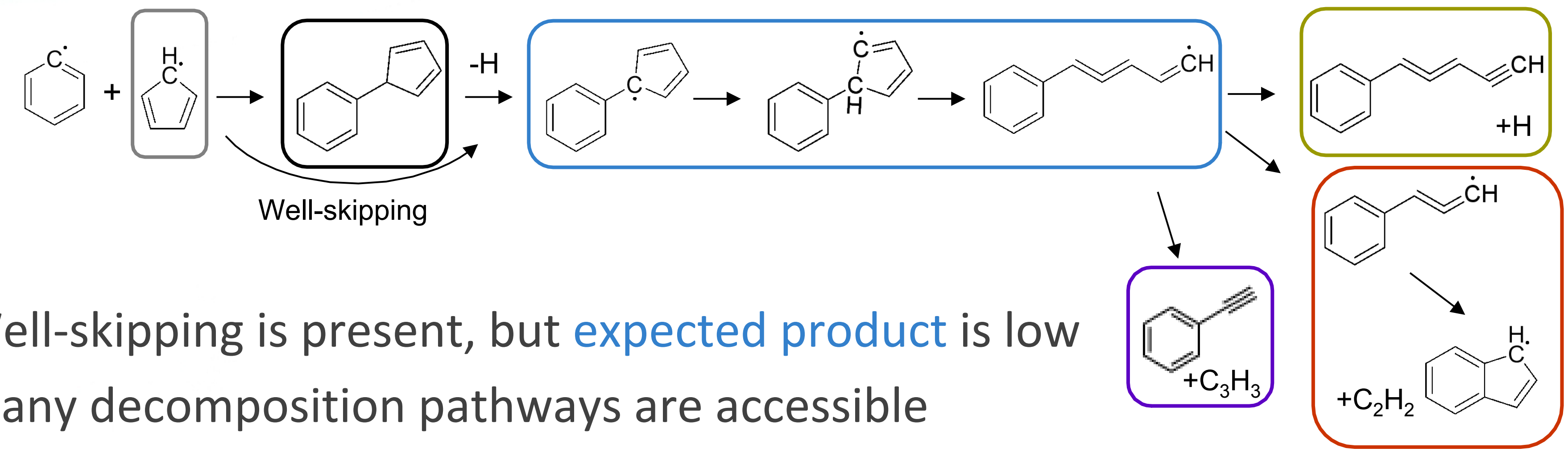
Phenyl + Cyclopentadienyl



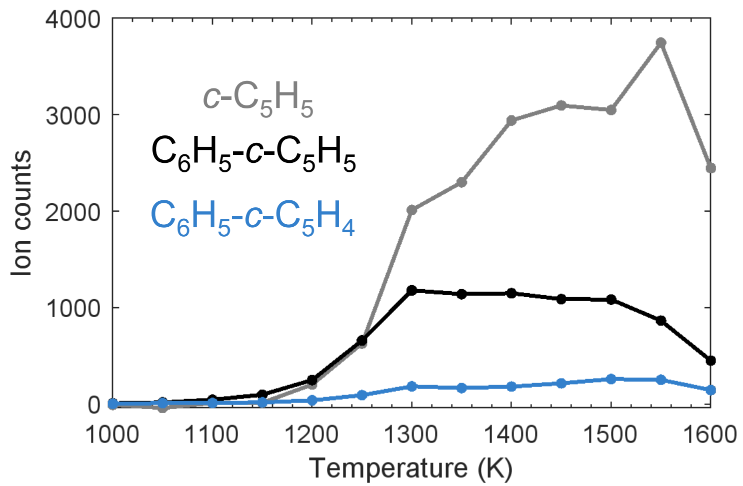
- Well-skipping is present, but expected product is low

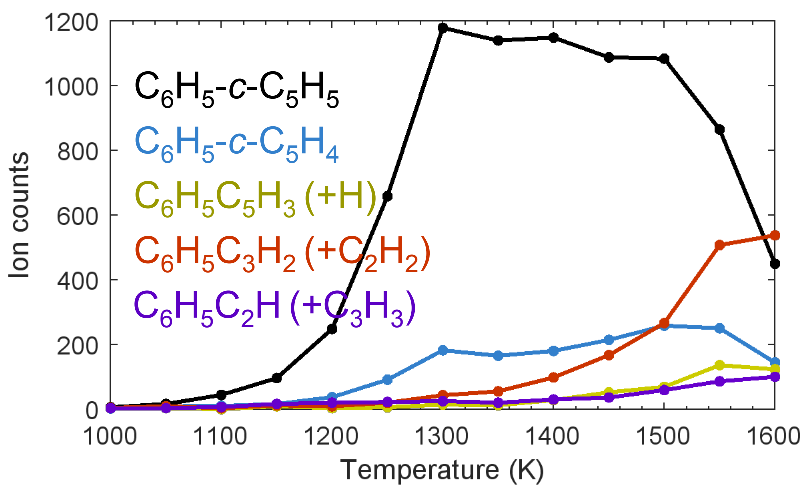


Phenyl + Cyclopentadienyl



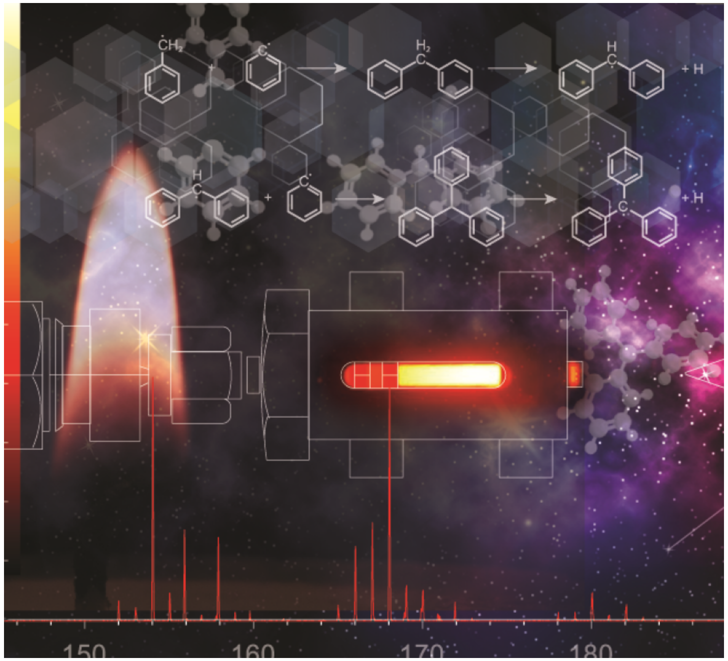
- Well-skipping is present, but expected product is low
- Many decomposition pathways are accessible





Conclusions

- σ-radical + π-radical reactions tend to produce 5-member-ring π-radicals
- The well-skipping routes can be significant at 30 Torr
- Radical-radical well-skipping is negligible at 1+ atm



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Implications of well-skipping

- Within soot community, well-skipping reactions are likely occurring in low-pressure flames that are often used to reduce complexity
- These well-skipping reactions probably are relevant to astrochemistry
  - PAHs form spontaneously at low pressures and low temperatures
- Could we grow carbon nanotubes or other particles by well-skipping reactions?
  - Requires occasional reactivation and low pressure
  - Allows C_3, C_6, or C_9 feedstocks
  - Makes imperfect structures, maybe useful as construction material

Acknowledgements

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Lawrence Livermore

Dr. Goutham Kukkadapu

Argonne

Dr. Ahren Jasper

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Summary

- We studied three σ-radical + π-radical reactions
  - All three showed well-skipping behavior
  - All three well-skipping products produced polycyclic hydrocarbon radicals containing a 5-member-ring
- Simulation reveals that well-skipping is negligible at atmospheric pressure but important at 30 Torr
  - Low pressure flame studies must consider well-skipping reactions
  - Radical-radical well-skipping may be dominant in extreme low pressure astrochemistry