Computational Study on the Recombination Reaction between Benzyl and Propargyl Radicals

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Outline

Introduction

- Background and motivation

- Computational methods

Benzyl + Propargyl

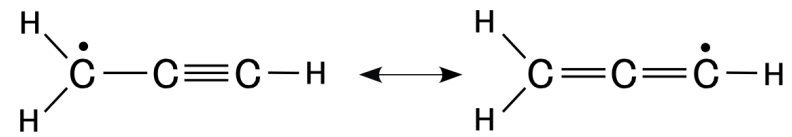- Reaction pathways

- Rate constants and products

Secondary Reactions

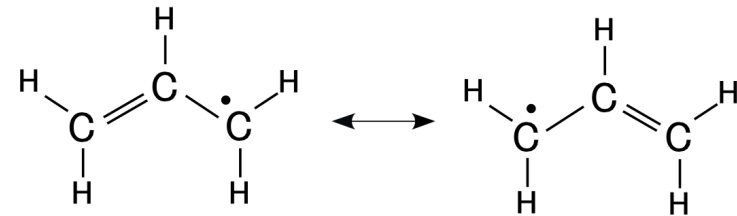- Decomposition of methylene-indanyl radical

Summary and Implication

Resonance-Stabilized Radicals (RSRs)

Delocalization of Unpaired Electron

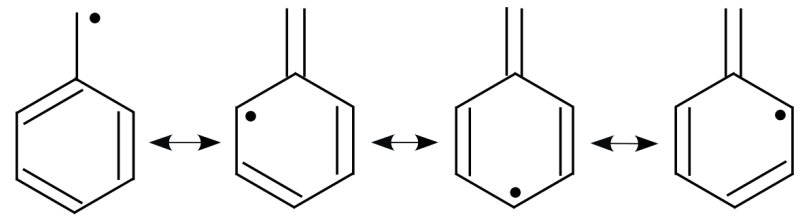Thermodynamically Stable

(Compared with localized radicals)

- Slow Reaction Rates with O_2
- Slow Decomposition Rates

⇩

Abundant in Combustion of Hydrocarbon Fuels

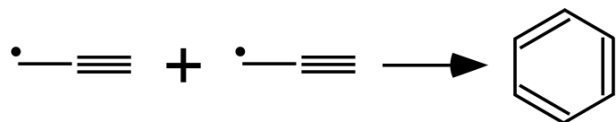Propargyl (C_3H_3)

Allyl (C_3H_5)

Benzyl (C_7H_7)

Recombination reactions between RSRs play significant roles in molecular-weight growth chemistry in combustion

Reactions Involving RSRs

Understanding the kinetics and mechanisms of reactions involving RSRs is essential for *quantitatively* predicting the PAHs (polycyclic aromatic hydrocarbons) formation and growth in combustion
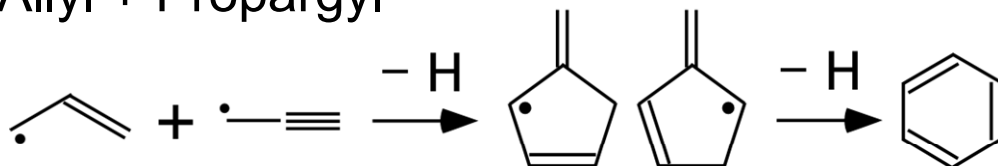
- Propargyl + Propargyl

Miller and Melius *Combust. Flame* **1992**
Miller and Klippenstein *J. Phys. Chem. A* **2003**
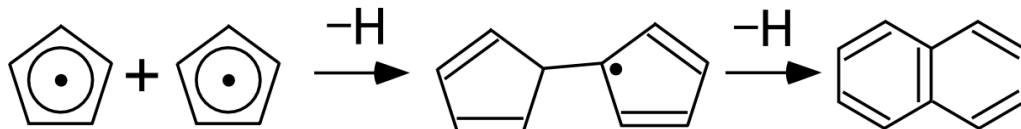
- Allyl + Propargyl

Marinov et al. *Combust. Sci. Tech.* **1997**
Miller et al. *J. Phys. Chem. A* **2010**
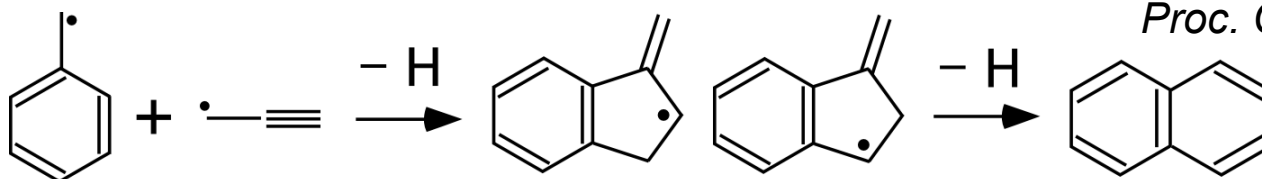Matsugi et al. *J. Phys. Chem. A* **2011**

- Cyclopentadienyl + Cyclopentadienyl

Melius et al. *Proc. Combust. Inst.* **1996**
Mebel and Kislov *J. Phys. Chem. A* **2009**

- Benzyl + Propargyl (**Present Work**)

Suggested by Marinov et al.
Proc. Combust. Inst. **1998**

Past Modeling Studies

Several past kinetic modeling studies highlighted the importance of benzyl + propargyl reaction for the formation of bi-cyclic species (*i.e.* naphthalene)

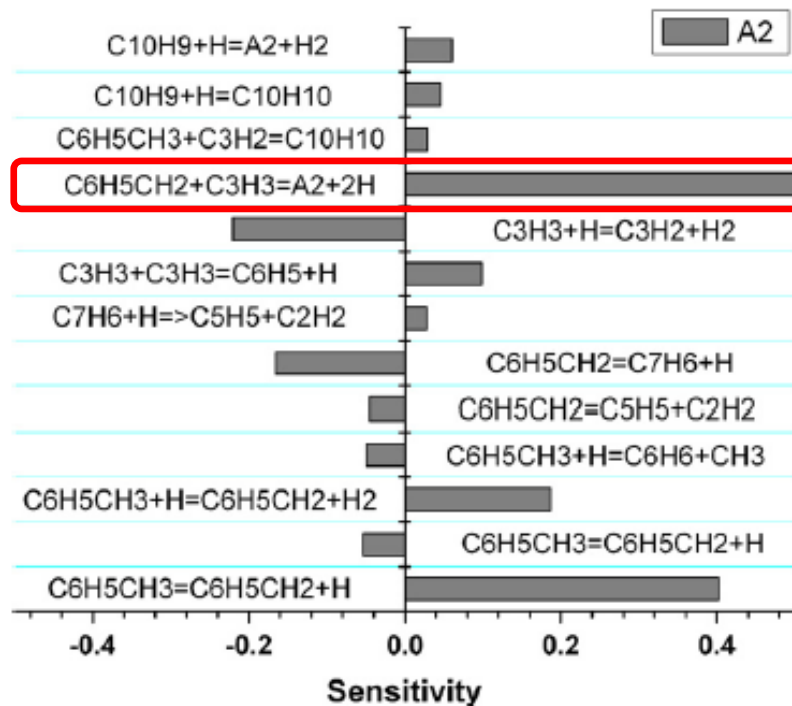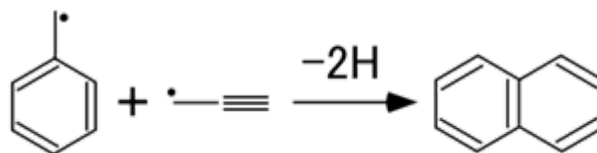|	
Methane flame	Marinov et al. *Proc. Combust. Inst.* **1998**
Propene flame	Kamphus et al. *Combust. Flame* **2008**
Toluene flame	Detilleux and Vandooren *J. Phys. Chem. A* **2009**
Methane/ethene flame	Slavinskaya and Frank *Combust. Flame* **2009**
Toluene pyrolysis	Zhang et al. *Combust. Flame* **2010**

S_{C10H8} in Toluene pyrolysis modeling at 1670 K

Zhang et al. *Combust. Flame* **2010**

was the most responsible source for producing $C_{10}H_8$

The Rate Constant for Benzyl + Propargyl

Previously Estimated $k_{benzyl+propargyl}$
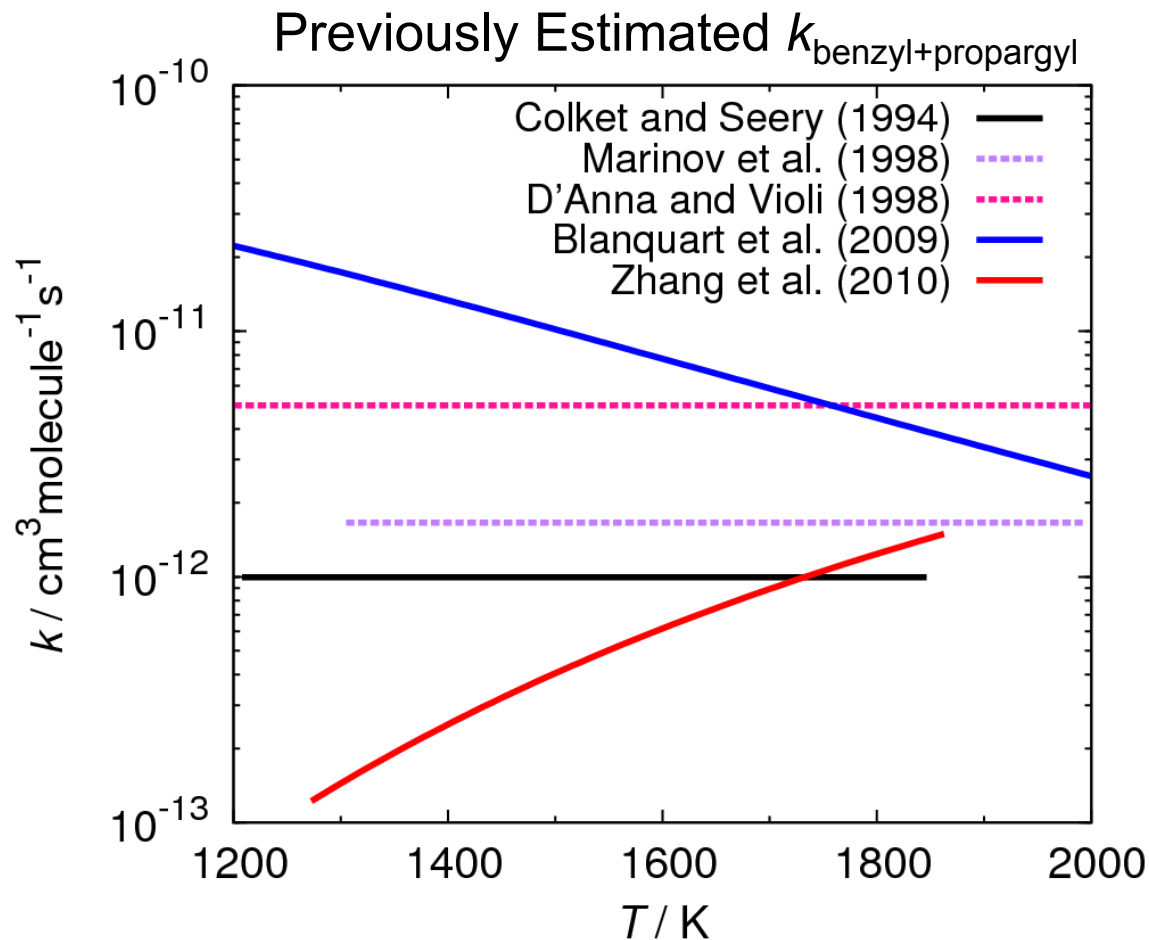
There have been **large variations in** $k_{benzyl+propargyl}$ used in the past studies

This Work:

Detailed computational investigation for benzyl + propargyl reaction to obtain reliable kinetic data

Computational Methods

Quantum Chemical Calculations by Gaussian 03 and Molpro 2008.1

- CBS-QB3 methods

- *Singlet-Triplet gap method* (with CASPT2) for diradicals

- CASPT2(10e10o)/vtz // UB3LYP/6-311G(d,p) for barrierless channels

TST & RRKM / Master-Equation Analysis

by UNIMOL / SSUMES programs
http://www.frad.t.u-tokyo.ac.jp/~miyoshi/ssumes/

- RRKM rate coefficient

   - Conventional TST calculation with 1D tunneling correction

   - Microcanonical variational TST calculation for barrierless recombination / dissociation

- Collisional energy transfer

   Single exponential down model: $\langle \Delta E_{\text{down}} \rangle = 400\,(T\,/\,300)^{0.7}\,\text{cm}^{-1}$

- Steady-state multiple-well master-equation analysis to compute product specific $k(T,p)$

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- Computational methods

Benzyl + Propargyl

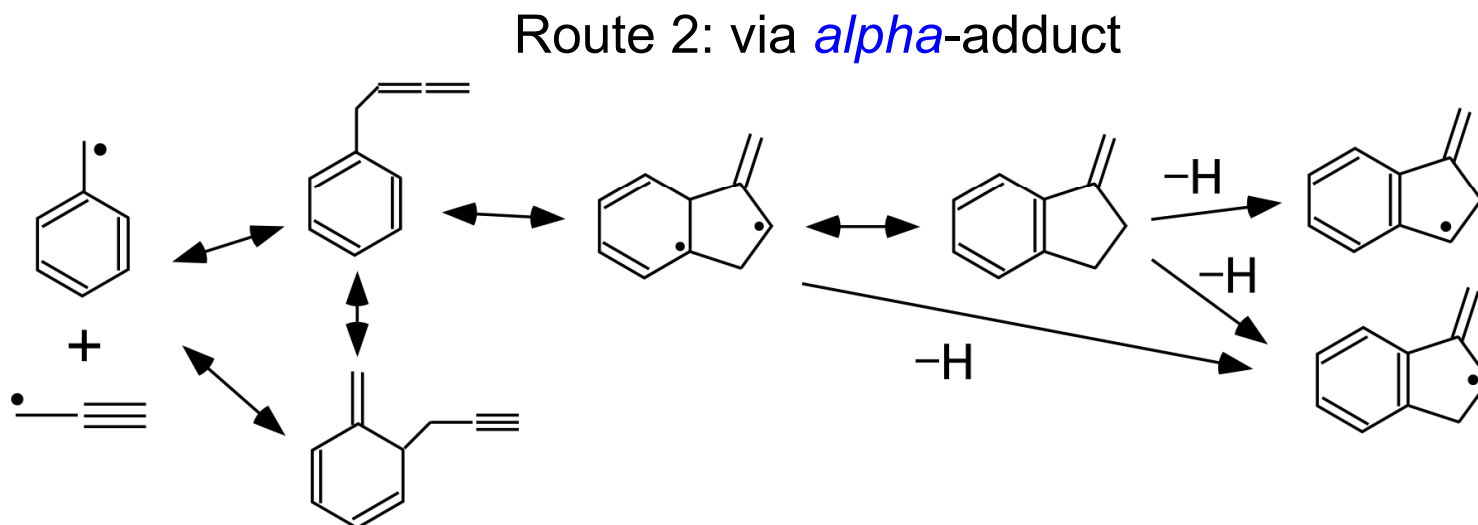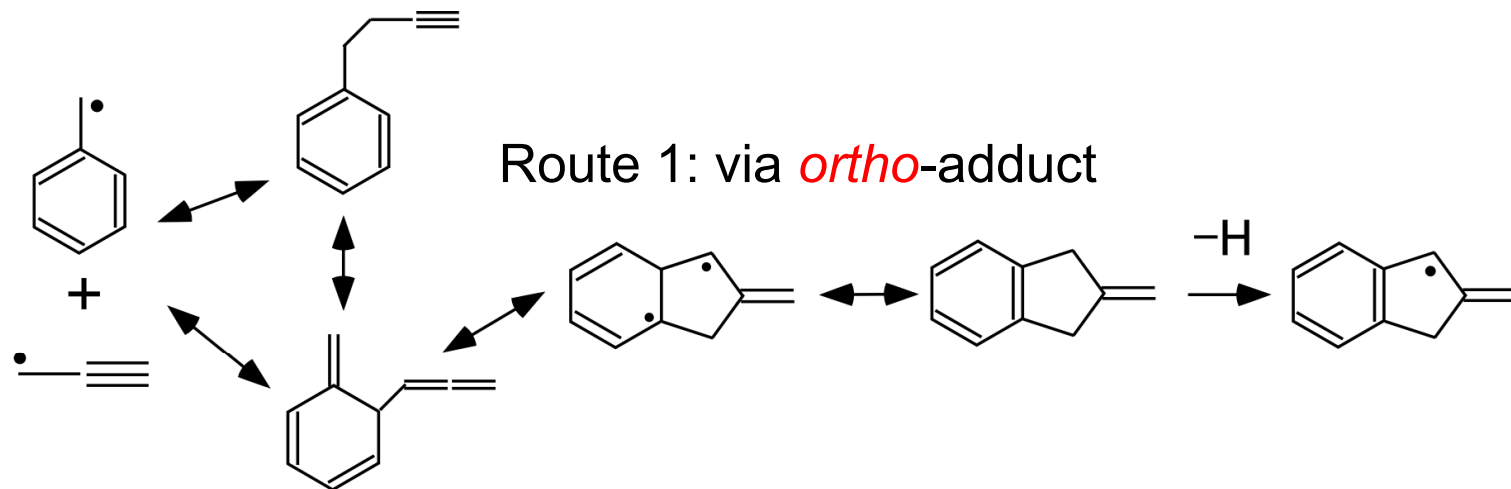**- Reaction pathways**

- Rate constants and products

Secondary Reactions

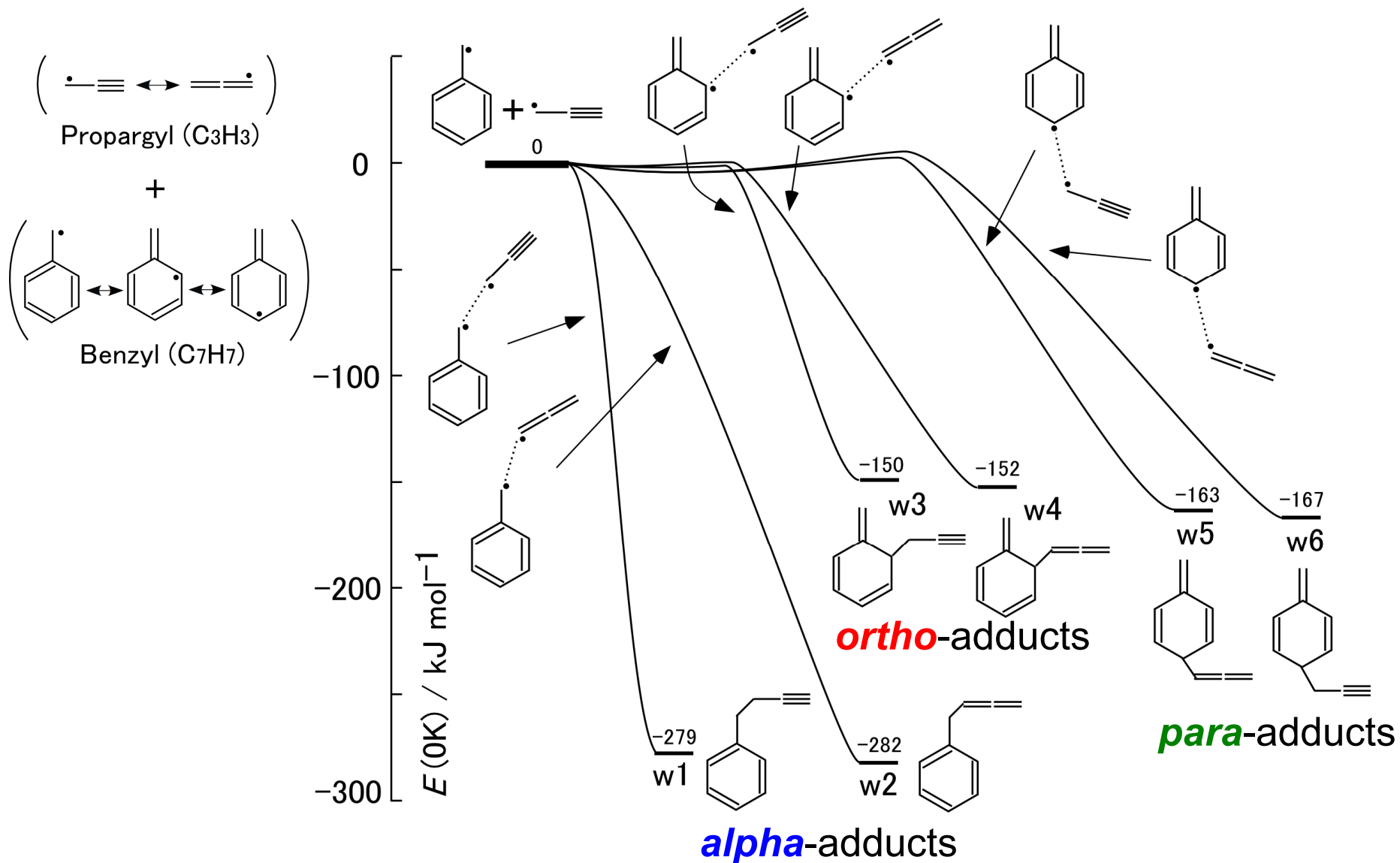- Decomposition of methylene-indanyl radical

Summary and Implication

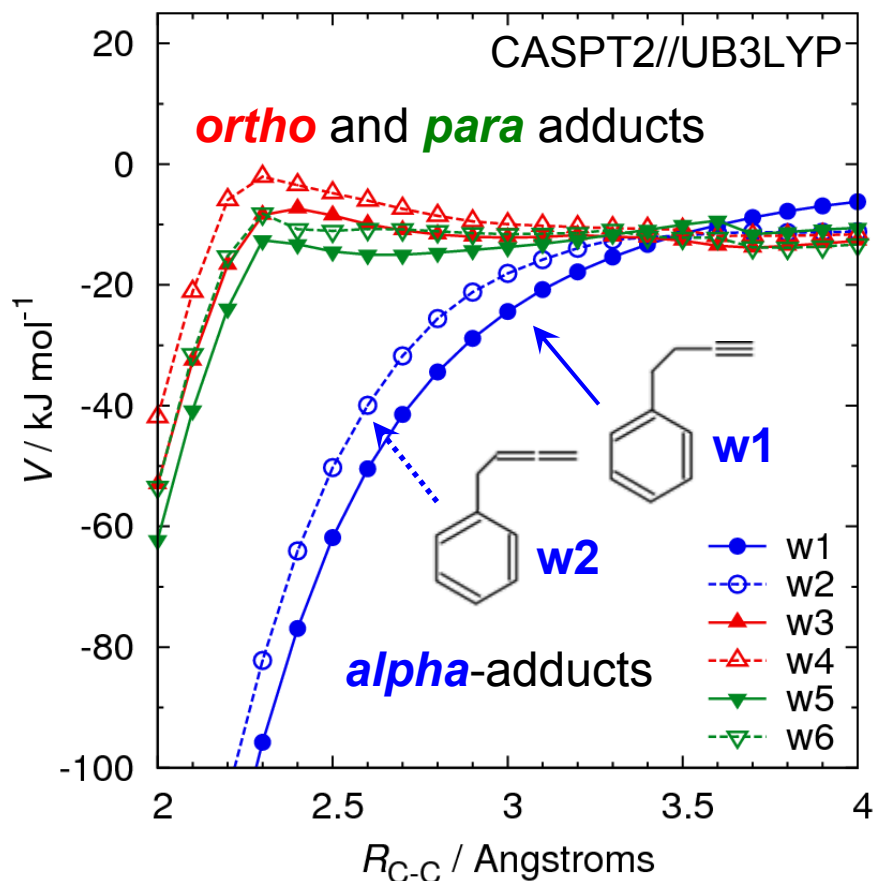# Benzyl + Propargyl:
Two Possible Bi-Cyclization Pathways

Route 1: via *ortho*-adduct

Route 2: via *alpha*-adduct

−H

−H

−H

−H

Both pathways involve the diradical intermediates

Entrance: Six Recombination Channels

Propargyl (C3H3)

+

Benzyl (C7H7)

$E(0K) / kJ mol^{-1}$

−100

−200

−300

0

−279
w1

−282
w2

−150
w3

−152
w4

−163
w5

−167
w6

ortho-adducts

alpha-adducts

para-adducts

Entrance: High-Pressure Limiting Rate Constants

Potential energy curves

VTST rate constants
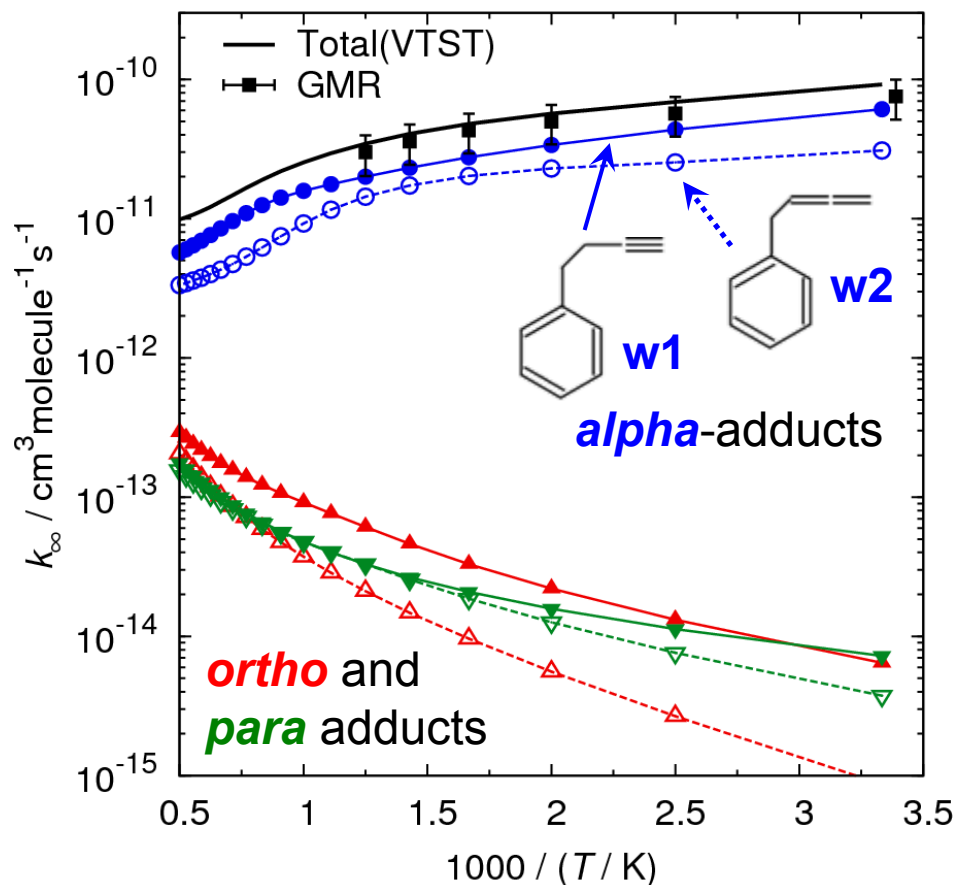
ΔV_{adj} = +3.0 kJ/mol (fitted to k^{GMR})
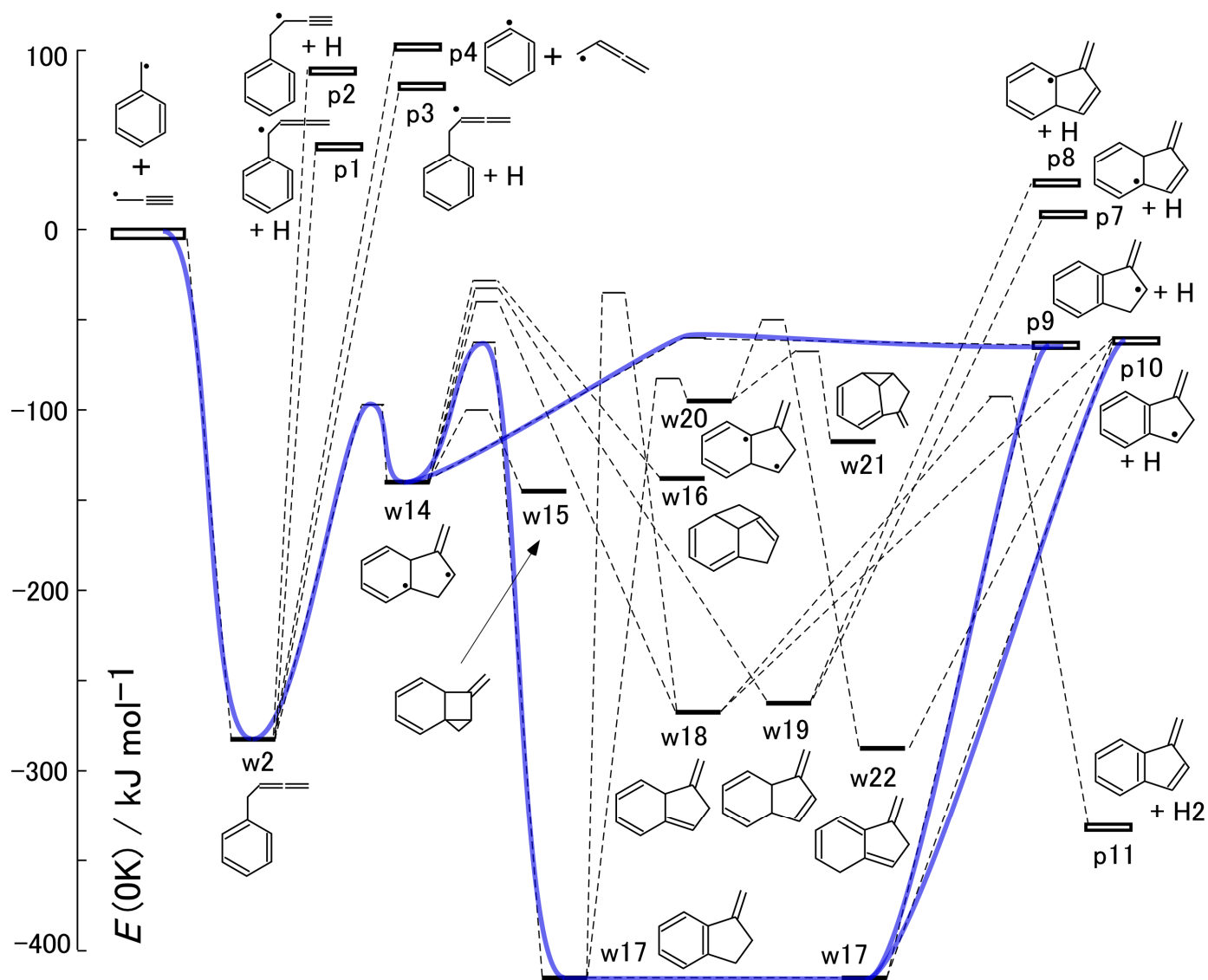
GMR: Geometric Mean Rule: $k^{GMR}_{C7H7+C3H3} = 2\sqrt{k_{C7H7+C7H7} k_{C3H3+C3H3}}$

Associations to the methylenic (*alpha*-) carbon sites are dominant

Energy Diagram: Bi-Cyclization Pathway 1
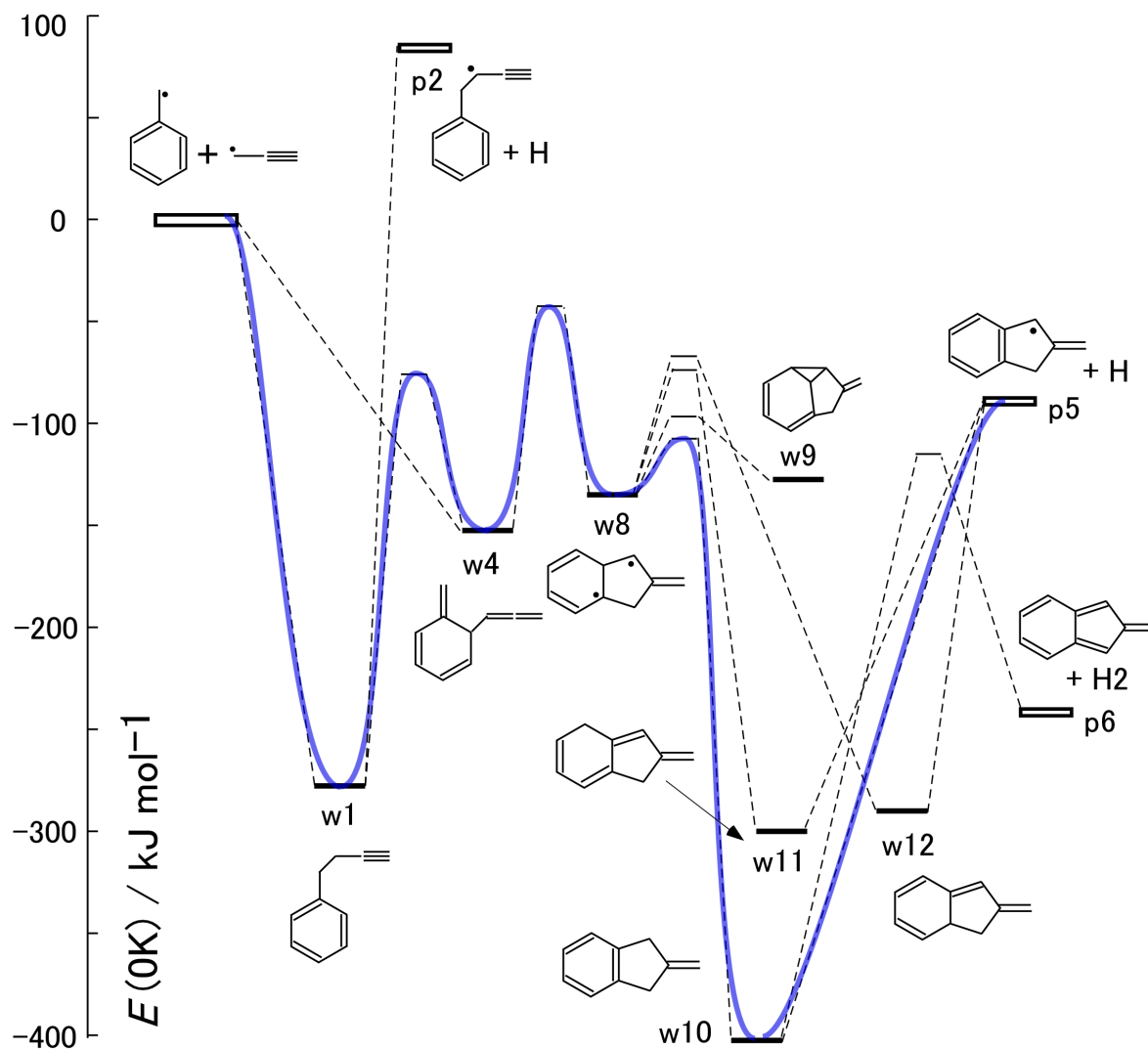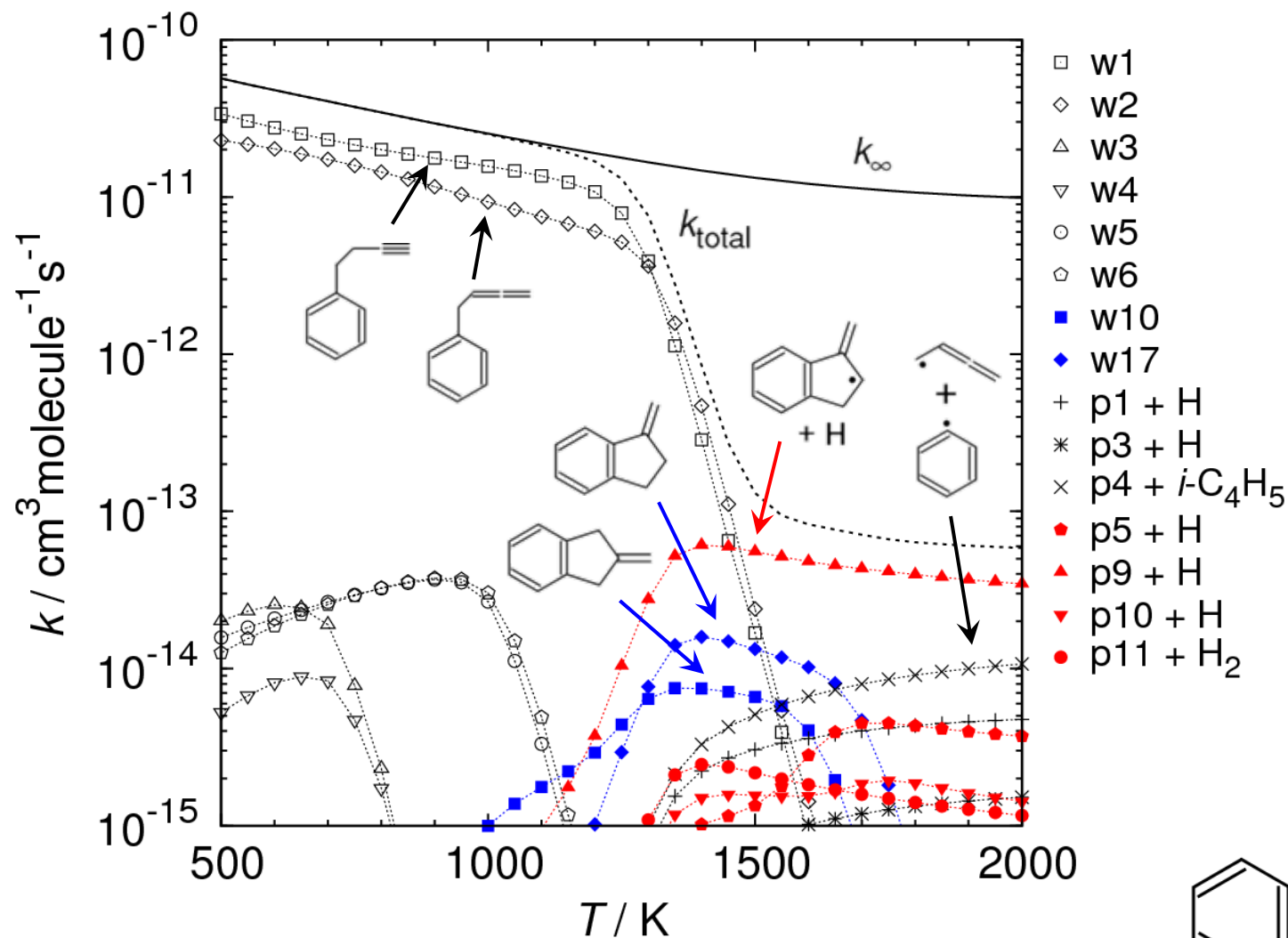
Energy Diagram: Bi-Cyclization Pathway 2
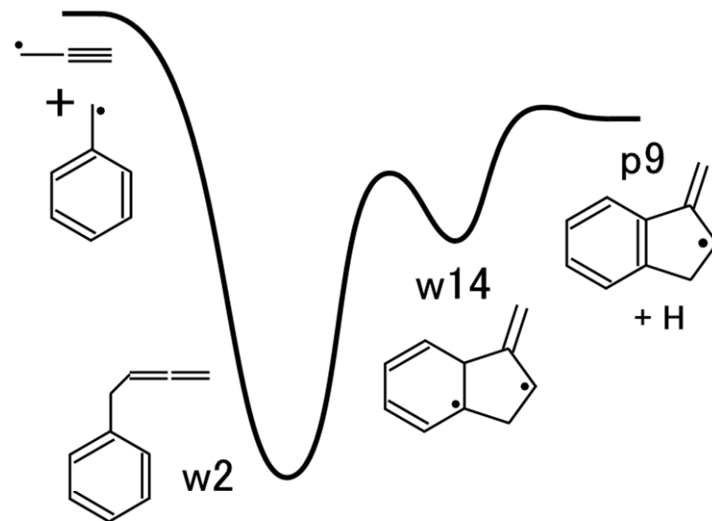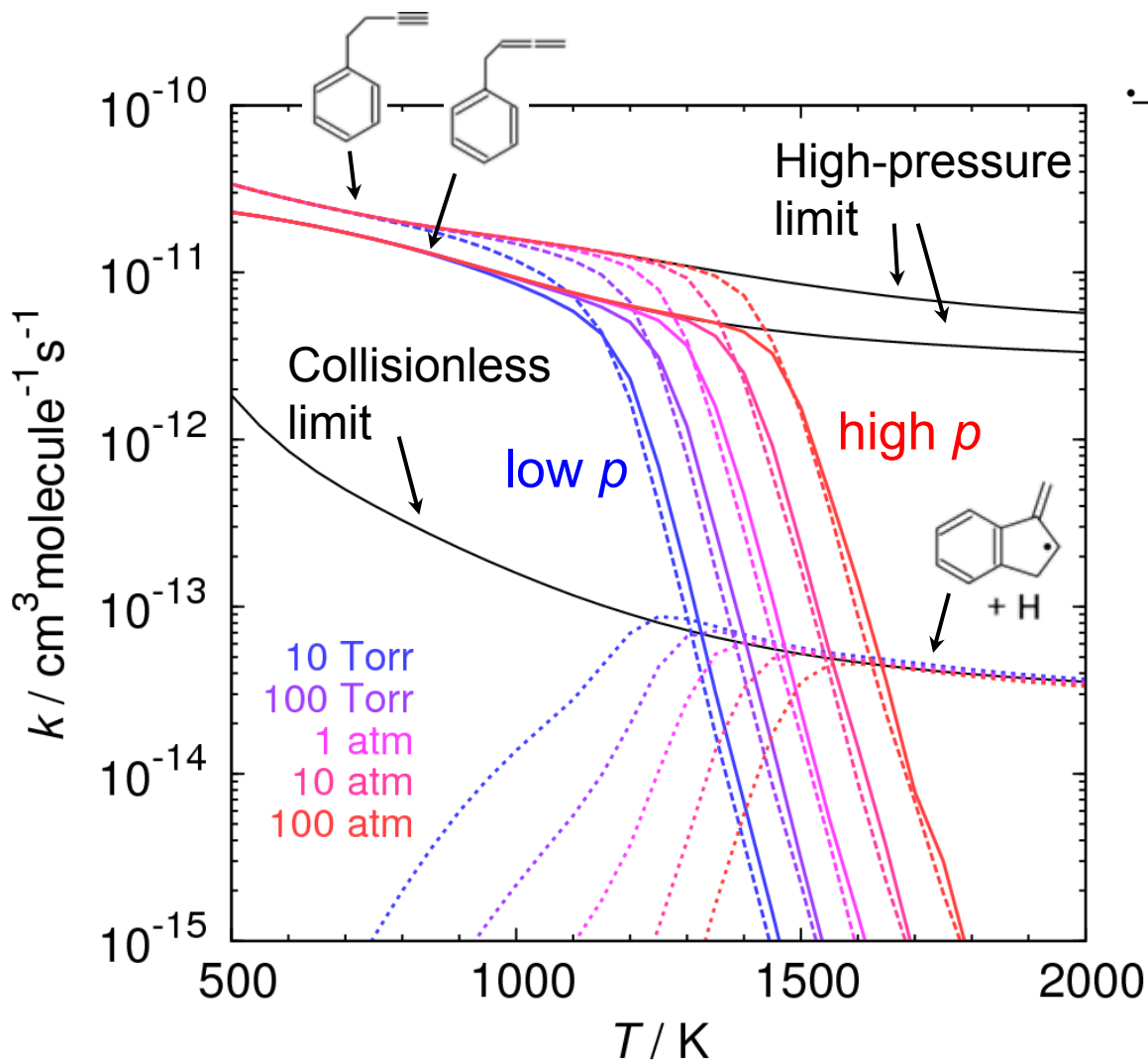
Products Specific Rate Constants

P_{total} = 1 atm (N_2)

Dominant product at high T: **1-methylene-2-indanyl radical (p9)**

Significant pressure fall-off effect (factor of ~100 at T > 1400 K)
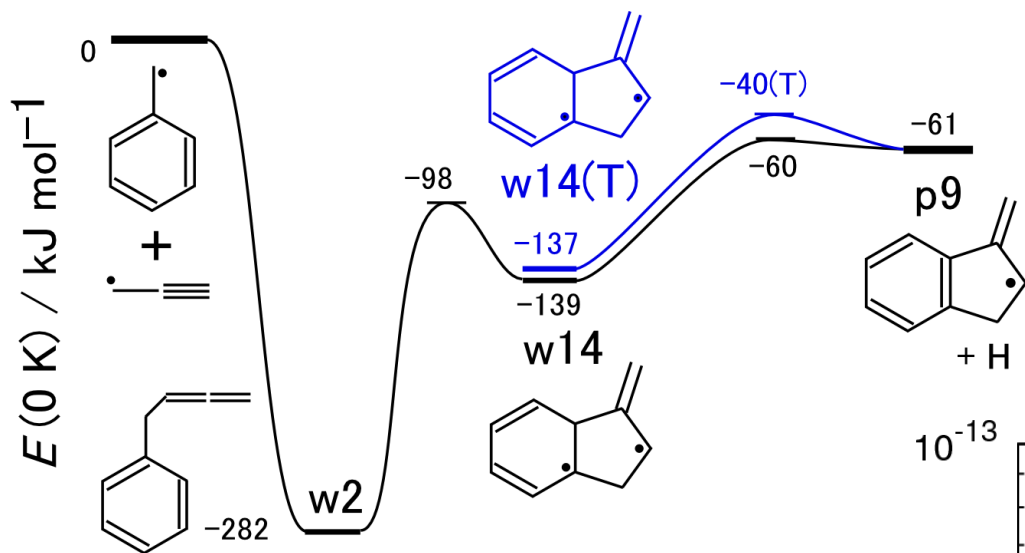
Pressure Dependence for Major Channels

Dissociations become dominant over collisional energy transfer at high T

$$\Rightarrow \quad k_{overall} \sim k_{p=0}$$
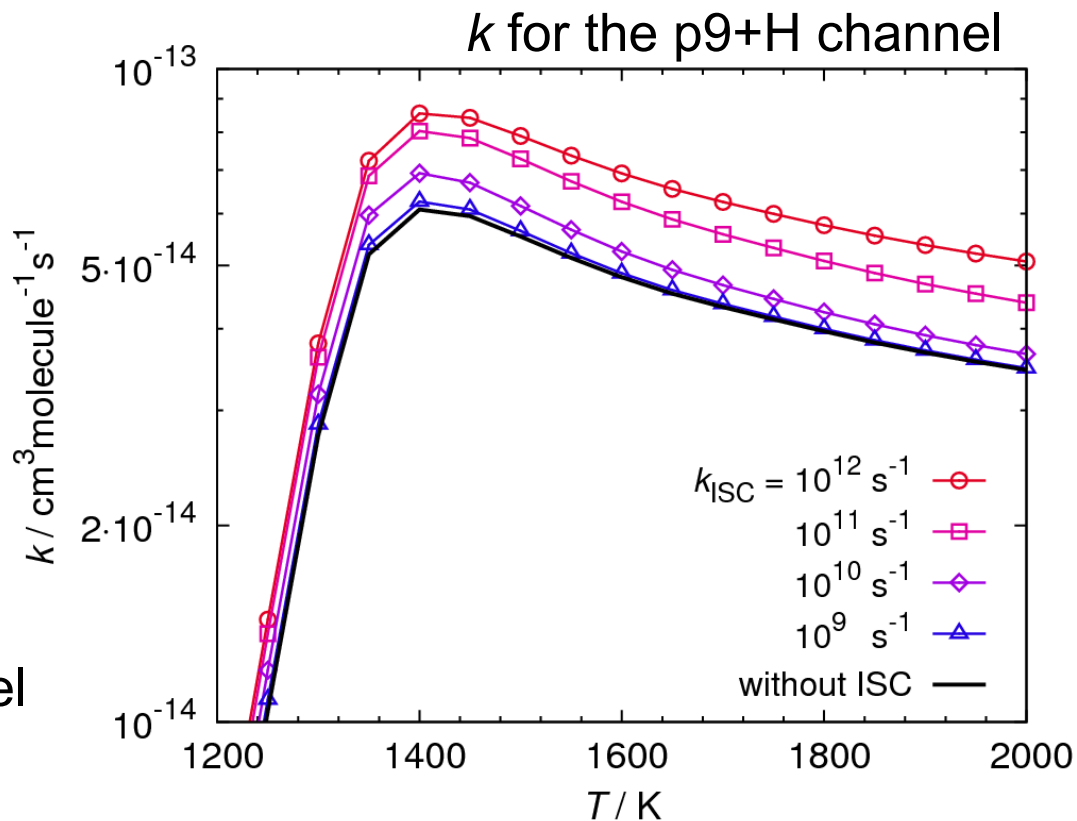
Possible Contributions of Triplet Pathway

H-elimination from the diradical can also occur on the triplet PES

- S-T energy gap = 1.7 kJ/mol

- MECP: 3.5 kJ/mol above S

- The PESs are almost parallel

  → Allow rapid intersystem crossing (ISC)

RRKM/ME calculation including the triplet pathway with *arbitrary* chosen ISC rate (k_{ISC})

ISC may results in at most ~50% acceleration of k for p9+H channel

k for the p9+H channel

$k_{ISC} = 10^{12}$ s^{-1}
10^{11} s^{-1}
10^{10} s^{-1}
10^{9} s^{-1}
without ISC

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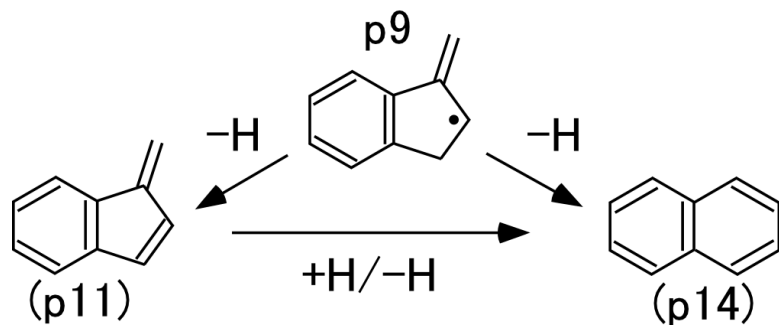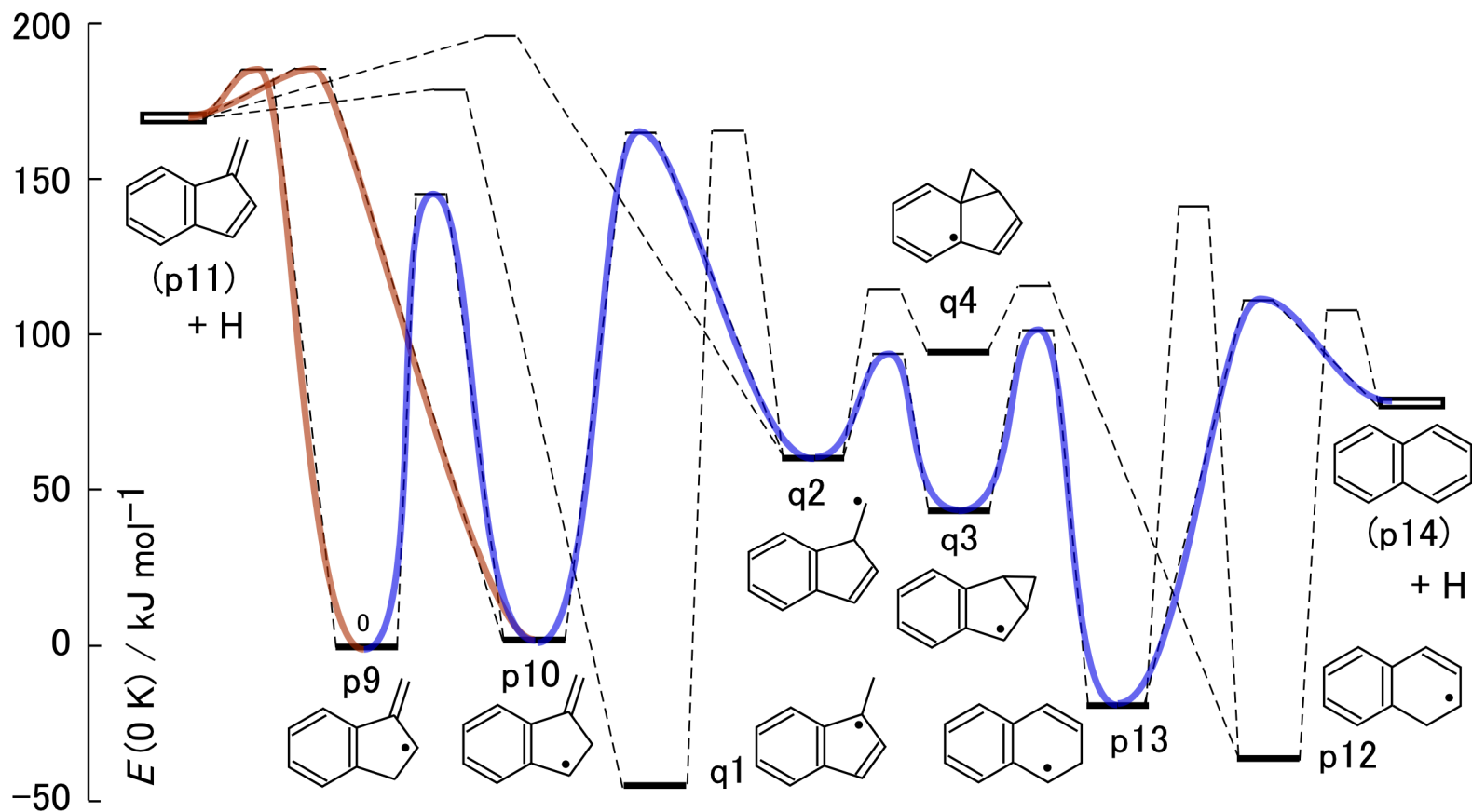   - Computational methods

Benzyl + Propargyl

    - Reaction pathways

    - Rate constants and products

Secondary Reactions

    - Decomposition of methylene-indanyl radical

Summary and Implication

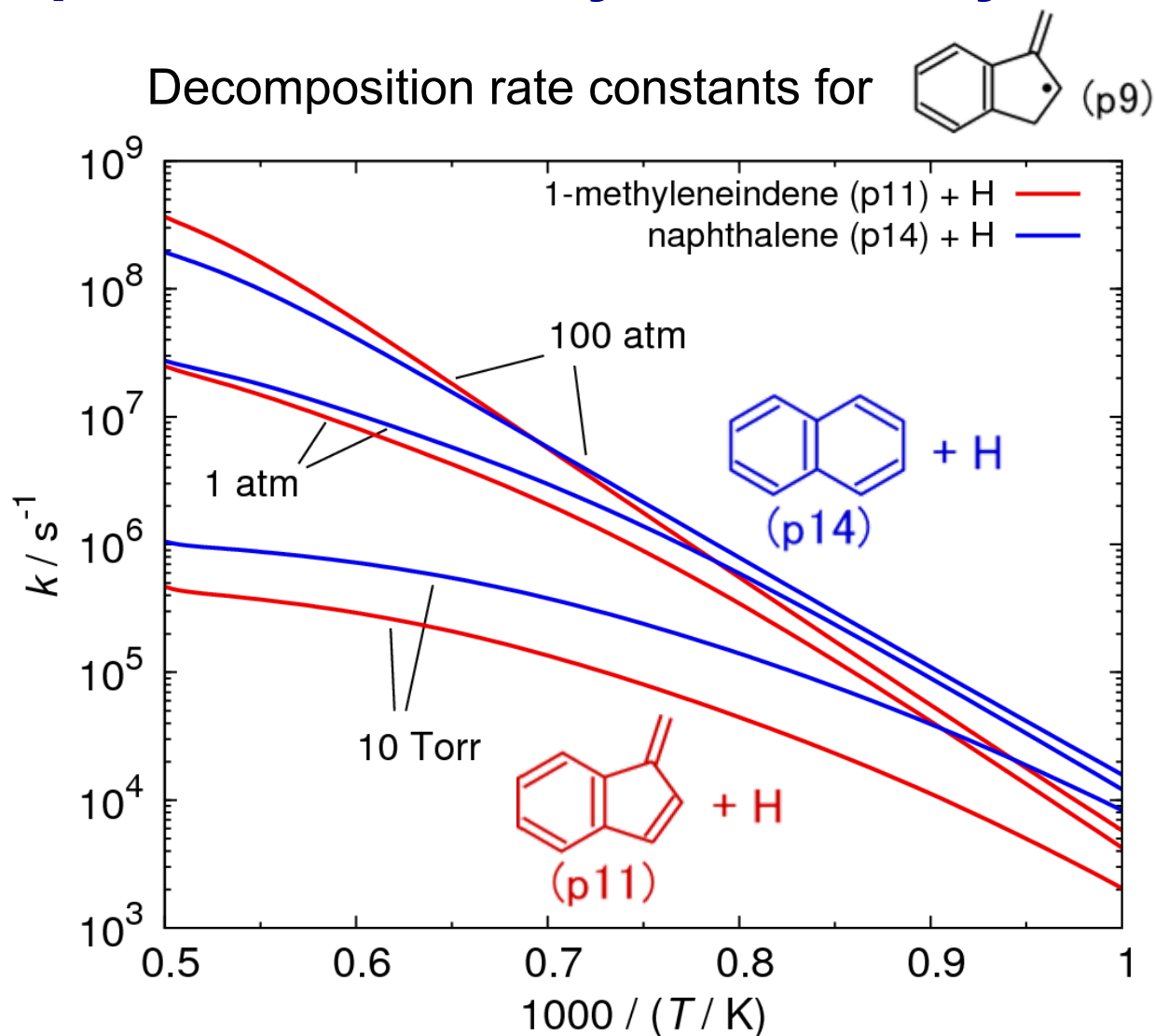# Fate of Methylene-indanyl radical

- p9 can decompose to p11 (methylene-indene) or to p14 (naphthalene)

- p11 can be converted to p14 via H-catalyzed isomerization

Decomposition of Methylene-indanyl radical

Decomposition rate constants for (p9)

The methylene-indanyl radicals rapidly decompose to produce either methylene-indene (p11) or naphthalene (p14)

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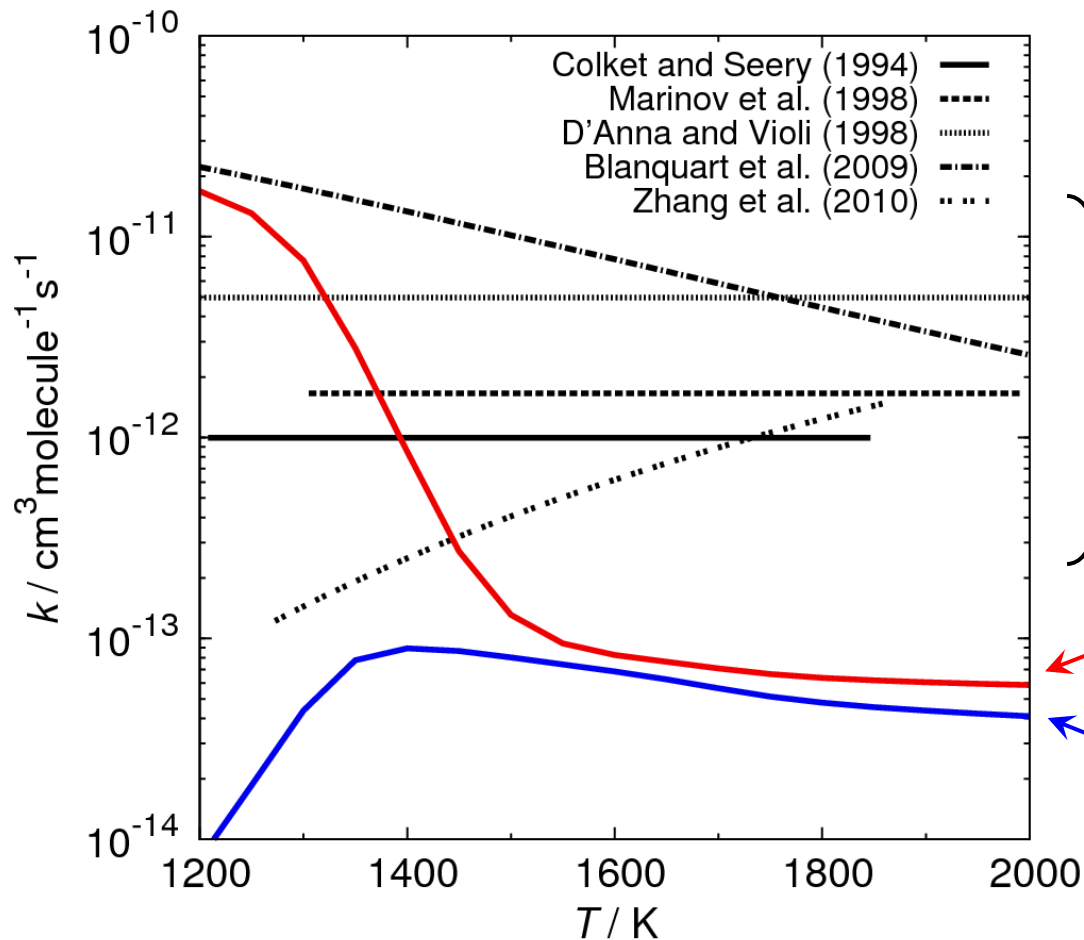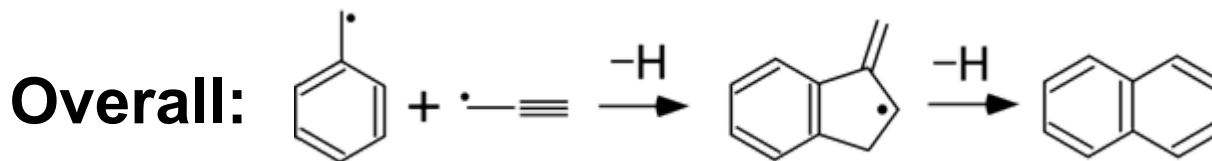
- Reaction pathways
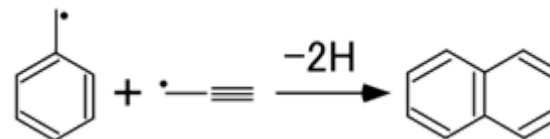
- Rate constants and products

Secondary Reactions

- Decomposition of methylene-indanyl radical

Summary and Implication

Overall Kinetics & Comparison

Summary

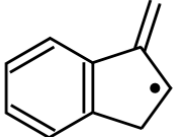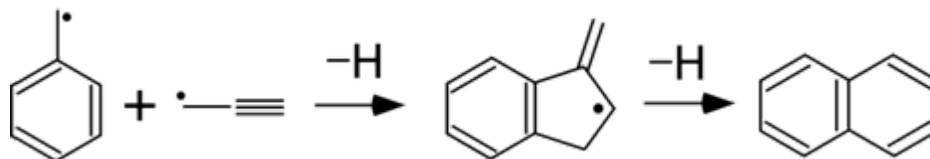Quantum chemical and RRKM / master-equation calculations were performed for the benzyl + propargyl recombination reaction.

- Major product: 1-methylene-2-indanyl radical

- Significant pressure fall-off effect at high T

- Quantitative kinetic mechanisms were constructed

$k_{benzyl+propargyl}$ used in the previous kinetic modeling studies were largely overestimated.

Reaction mechanisms for the formation of naphthalene in combustion should be revised.