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)

\[
\begin{align*}
\text{Slow Reaction Rates with O}_2 \\
\text{Slow Decomposition Rates}
\end{align*}
\]

Abundant in Combustion of Hydrocarbon Fuels

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
  \[
  \cdot \equiv + \cdot \equiv \rightarrow \text{Cyclopentadienyl}
  \]
  Miller and Melius *Combust. Flame* 1992

- Allyl + Propargyl
  \[
  \cdot \equiv + \cdot \equiv \rightarrow \text{Cyclopentadienyl} \rightarrow \text{Cyclopentadienyl}
  \]

- Cyclopentadienyl + Cyclopentadienyl
  \[
  \text{Cyclopentadienyl} \rightarrow \text{Cyclopentadienyl} \rightarrow \text{Cyclopentadienyl}
  \]

- Benzyl + Propargyl (Present Work)
  \[
  \text{Benzyl} + \cdot \equiv \rightarrow \text{Cyclopentadienyl} \rightarrow \text{Cyclopentadienyl}
  \]
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
- Propene flame
- Toluene flame
- Methane/ethene flame
  - Slavinskaya and Frank *Combust. Flame* 2009
- Toluene pyrolysis
  - Zhang et al. *Combust. Flame* 2010

\[ S_{C_{10}H_8} \text{ in Toluene pyrolysis modeling at 1670 K} \]

Zhang et al. *Combust. Flame* 2010

\[
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_3\text{H}_3 = \text{A}_2 + 2\text{H} \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_3\text{H}_3 = \text{A}_2 + 2\text{H} \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_3\text{H}_3 = \text{A}_2 + 2\text{H} \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_3\text{H}_3 = \text{A}_2 + 2\text{H} \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_3\text{H}_3 = \text{A}_2 + 2\text{H} \\
\]

\[-0.4 \quad -0.2 \quad 0.0 \quad 0.2 \quad 0.4\]

Sensitivity

\[
\text{1}^* + \text{---} \rightarrow \text{2H} \rightarrow \text{C}_8\text{H}_{10} \\
\]

was the most responsible source for producing \( C_{10}H_8 \)
The Rate Constant for Benzyl + Propargyl

There have been large variations in $k_{\text{benzyl+propargyl}}$ 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: $\langle \Delta E_{\text{down}} \rangle = 400 \left( \frac{T}{300} \right)^{0.7}$ cm$^{-1}$
- Steady-state multiple-well master-equation analysis to compute product specific $k(T,p)$
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Summary and Implication
Benzyl + Propargyl: Two Possible Bi-Cyclization Pathways

Route 1: via ortho-adduct

Route 2: via alpha-adduct

Both pathways involve the diradical intermediates
Entrance: Six Recombination Channels

Propargyl (C₃H₃)

Benzyl (C₇H₇)

α-adducts

ortho-adducts

para-adducts

E(0K) / kJ mol⁻¹
Entrance: High-Pressure Limiting Rate Constants

Potential energy curves

CASPT2//UB3LYP

ortho and para adducts

\( \Delta V_{adj} = +3.0 \text{ kJ/mol (fitted to } k^{GMR} \) \\

GMR: Geometric Mean Rule: 

\[
k^{GMR}_{C_7H_7+C_3H_3} = 2\sqrt{k_{C_7H_7+C_7H_7} k_{C_3H_3+C_3H_3}}
\]

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

$P_{\text{total}} = 1 \text{ atm (N}_2)$

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

Significant pressure fall-off effect (factor of $\sim 100$ at $T > 1400 \text{ K}$)
Pressure Dependence for Major Channels

Dissociations become dominant over collisional energy transfer at high $T$

$\Rightarrow k_{\text{overall}} \sim k_{p=0}$
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
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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

The methylene-indanyl radicals rapidly decompose to produce either methylene-indene (p11) or naphthalene (p14).
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Summary and Implication
Overall Kinetics & Comparison

Overall: \( \text{C}_{6}H_{5}^* + \cdot \equiv \rightarrow \text{C}_{10}H_{10} - \text{H} \rightarrow \text{C}_{10}H_{8} \)

Previous estimations

This work, Total (1 atm)

This work, Bi-cyclics (1 atm)
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

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

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