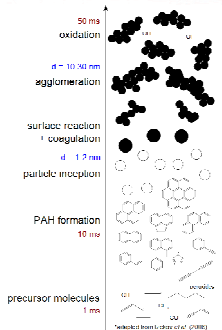


# Kinetics and isomer-resolved product distributions from the cyclopentadienyl radical self-reaction

SAND2010-4782P

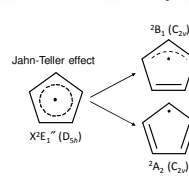
John D. Savee, Talitha M. Selby, Satchin Soorkia, Adam J. Trevitt, Craig A. Taatjes, and David L. Osborn  
Combustion Research Facility, Sandia National Laboratories, Mail Stop 9055,  
Livermore, CA 94551-0969 USA

## Molecular Weight Growth Chemistry



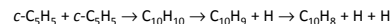
- Soot particles are an unwanted byproduct of combustion
- Carcinogenic and mutagenic properties
- Global warming implications
- Reduction of engine efficiency
- Particulation begins with polyaromatic hydrocarbon (PAH) formation – fuel specific
- Pathways leading to initial PAH species in aliphatic fuels debated
  - radical + radical vs. radical + closed-shell reactions
  - rate determining step in soot formation?
- Flame speciation is complex; isomeric resolution important

## Cyclopentadienyl ( $C_5H_5$ ) Radical Self-Reaction

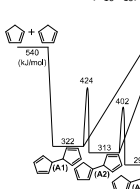


- Resonance-stabilized radical – ubiquitous in flames
- $C_3H_4 + C_2H_2 \rightarrow C-C_5H_6 \rightarrow C-C_5H_5 + H$
- $C_3H_3 + C_2H_2 \rightarrow C-C_5H_5$
- decomposition of aromatic fuels

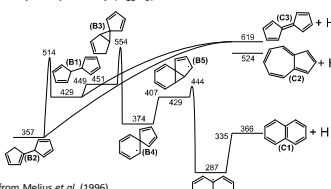
Potential naphthalene pathway:



Initial adduct ( $C_{10}H_{10}$ ):



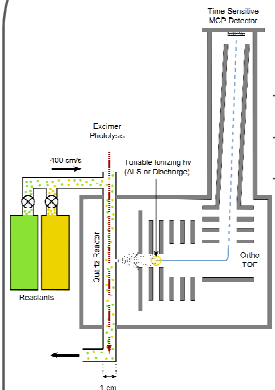
Spiran pathway ( $C_{10}H_9$ ):



\*Adapted from Melius et al. (1996)

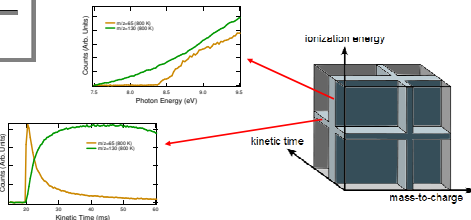
- Barrierless formation of initial adduct (9,10-dihydrofulvalene, A1)
- Subsequent H-loss and isomerization to hydrofulvalenyl (B1, B2) and hydronaphthyl (B6) species
- Naphthalene (C1), azulene (C2), and fulvalene (C3) deepest wells on  $C_{10}H_8$  potential energy surface (PES)
- Extensive work done on  $C_{10}H_{11}$ ,  $C_{10}H_{10}$ ,  $C_{10}H_9$ , and  $C_{10}H_8$  PESs by A.M. Mebel and coworkers

## Multiplexed Photoionization Mass Spectrometry



- Reactions initiated via photolysis in quartz reactor:
 
$$C-C_5H_6 + 248 \text{ nm} \rightarrow C-C_5H_5 + H$$

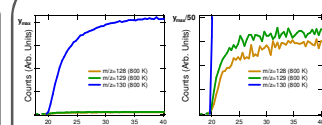
$$\rightarrow C_3H_3 + C_2H_3$$
- Reaction products sampled through 600  $\mu\text{m}$  pinhole
- Isomeric identification with tunable synchrotron radiation (ALS)
- Multiplexed data provides two-dimensional data for a single mass
- Yield vs. post-photolysis time ("kinetic time")  $\rightarrow$  kinetic information
- Photoionization efficiency (PIE)  $\rightarrow$  product identification



## CBS-QB3 Calculations of Ionization Potentials

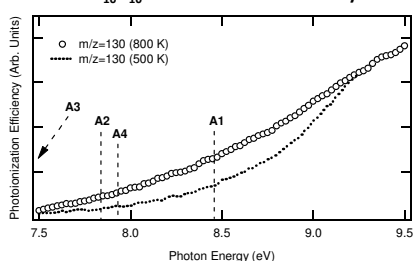
$C_{10}H_{10}$	trans / cis CBS-QB3 IP (eV)	$C_{10}H_9$	trans / cis CBS-QB3 IP (eV)
A1	8.46 / 8.00	B1	7.25 / 7.25
A2	7.84	B2	7.18
A3	7.21 / 7.16	B3	-
A4	7.93	B4	-
		B5	-
		B6	6.51 / 6.50
		B7	7.18
		B8	7.25
$C_{10}H_8$	CBS-QB3 IP (eV)	Lit. IP (eV)	
C1	8.17	8.14	
C2	7.51	7.42	
C3	8.22	-	

## Kinetic Traces



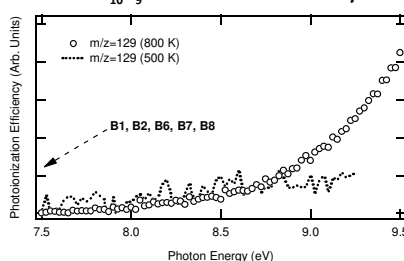
- Consistent with  $C_{10}H_{10} \rightarrow C_{10}H_9 \rightarrow C_{10}H_8$
- Self-rxn kinetics difficult – side reactions

## $C_{10}H_{10}$ Photoionization Efficiency



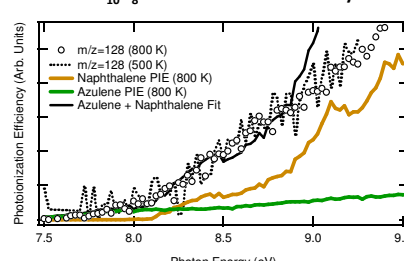
- High  $m/z = 130$  signal at both 500 and 800 K
- Temperature dependence seen in PIE curves  $\rightarrow$  different product distributions
- No clear onsets for new isomers above 7.5 eV – dense product distribution?
- Signal observed below 7.5 eV; A3 is only species found with IP < 7.5 eV

## $C_{10}H_9$ Photoionization Efficiency



- High  $m/z = 129$  signal at 800 K, almost no signal at 500 K
- All calculated  $C_{10}H_9$  IPs below 7.5 eV – difficult to interpret PIE curve

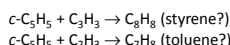
## $C_{10}H_8$ Photoionization Efficiency



- Low  $m/z = 128$  signal at both 500 and 800 K
- Poor fit of 800 K data to naphthalene + azulene PIE curves
- Need to consider other isomers – fulvalene (C3, IP = 8.22 eV)
- Observed  $C_{10}H_8$  signal may not be  $C_{10}H_{10} \rightarrow C_{10}H_8$  intermediate

## Future Directions

- Ab initio* simulations of PIE spectra under the Franck-Condon approximation
- Determination of photodissociation yields  $\rightarrow$  radical concentrations, kinetic insight
- Investigation into other reactions initiated by 248 nm photolysis of  $C-C_5H_6$ :



## Acknowledgements



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