

Reaction of cyclopentadiene with $\text{CH}(\text{X}^2\Pi)$ radicals, a new route toward the formation of benzene

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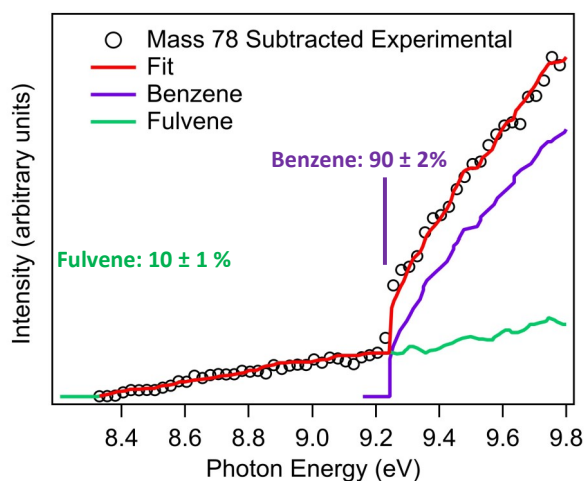
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General aspects

In the present work we investigated the reaction of cyclopentadiene (C_5H_6) with the combustion relevant radical CH leading to the formation of C_6H_6 isomers identified as fulvene and benzene. The formation of these aromatic ring molecules has been characterized experimentally using the kinetic apparatus from the chemical dynamics beamline at the Advanced Light Source, completed by computational investigation of PES. This study provides new valuable insight into the mechanism behind the formation of benzene and fulvene in carbon rich environments.



Photoionization spectrum of mass 78 produced by reaction between cyclopentadiene and CH

Cyclopentadiene (C_5H_6) has been detected in flames and is a key five-member ring intermediate in many high-temperature reactions such as toluene and benzyl pyrolysis.^{1,2} Recently it has been shown to be a major product during the pyrolysis of jet fuel JP-10.³ Cyclopentadiene reactions with abundant radicals have been proposed to play an important role during the formation of large polycyclic aromatic hydrocarbons (PAHs), such as naphthalene and indene.^{2,4-7} Because PAHs are potential precursors to soot, understanding the initial steps of aromatic molecule formation is vital toward reducing carbon emission during combustion processes.

Using the experimental setup at the ALS⁸, we were able to measure rate coefficients and branching ratios for the reactions of cyclopentadiene with $\text{CH}(\text{X}^2\Pi)$. Briefly, a gaseous mixture of cyclopentadiene obtained by thermal cracking of the dimer is introduced into the side sampling

flow tube. The adjustable kinetic time is 100 ms, the temperature ranges between 300 and 800K, the pressure between 2 and 8 mbar. The CH ($X^2\Pi$) free radicals are generated by photodissociation of bromoform (CHBr_3) by an excimer laser at 254 nm. After sampling, the molecules are ionized by a VUV radiation from the synchrotron. Reactant, intermediates and products are detected via a time-of-flight mass spectrometer. Finally, the intensity of the signal is recorded as a function of the molecular weight, the reaction time and the photoionization energy. Information about the reaction products is inferred by analyzing the time and mass dependent photoionization spectra. Isomers are identified by their photoionization energy and by fitting the experimental spectra with experimental or simulated reference spectra⁹⁻¹¹.

The data show that cycloaddition is the most likely entrance channel. Following the barrier-less addition, the bicyclic reaction intermediate can either ring open to give the resonance stabilized C_6H_7 radical or isomerize through transfer of a hydrogen atom from the sp^3 carbon of cyclopentadiene to the carbon from the initial CH radical. The 6-member ring intermediate can then directly decompose to give benzene and a H-atom. The initial intermediate may also lead to fulvene through ring opening and H-elimination. Transition states are computed and we suggest a mechanism to fully characterize this reaction¹².

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