

Supporting Information

Hydrogen-Abstraction/Acetylene-Addition Exposed

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Materials & Methods

Experiments were carried out at the Chemical Dynamics Beamline (9.0.2) of the Advanced Light Source in the Lawrence Berkeley National Laboratory. Employing a resistively-heated high-temperature silicon carbide (SiC) tube (chemical reactor), the molecular beam apparatus is equipped with a Wiley-McLaren Reflectron Time-of-Flight Mass Spectrometry (Re-TOF-MS). The chemical reactor mimics combustion-like conditions such as temperature and pressure along with chemical reactions to synthesize PAHs *in situ* involving reactions of combustion-relevant radicals. Here, styrenyl or *ortho*-vinylphenyl radicals (C_8H_7) were generated *in situ* via pyrolysis of β -bromostyrene or 2-bromostyrene (C_8H_7Br ; Sigma Aldrich) seeded in neat acetylene or helium gases of 400 Torr at a temperature of $1,500 \pm 50$ K, respectively. The concentrations of β -bromostyrene/2-bromostyrene in acetylene/helium were estimated to be less than 0.1% with a residence time of a few tens of microseconds.^[1-2] The temperature of the SiC tube was monitored using a Type-C thermocouple. The acetylene did not only act as a carrier gas, but also as a reactant with the pyrolytically generated radicals. Reaction products generated in the reactor were expanded supersonically and passed through a 2 mm diameter skimmer located 10 mm downstream and into the main chamber which houses the Re-TOF-MS. The quasi-continuous tunable vacuum ultraviolet (VUV) light from the Advanced Light Source intercepted the neutral molecular beam in the extraction region of the Re-TOF-MS. VUV single photon ionization profits from fragment-free ionization and hence is defined as a soft ionization method in contrast to electron impact ionization, which often results in excessive fragmentation of the parent ion. The ions formed via photoionization were then extracted perpendicularly to the molecular beam and fed into a microchannel plate detector by an ion lens. Photoionization efficiency (PIE) curves, which report ion counts as a function of photon energy at a particular mass-to-charge ratio (m/z), were extracted by integrating the signal recorded at the specific m/z over the energy range 8.00 to 11.00 eV in an increment of 0.05 eV and normalized to the photon flux. We also conducted blank experiments by expanding only acetylene carrier gas into the resistively-heated SiC tube and by replacing acetylene with helium carrier gas. No naphthalene reaction products were detected in these control experiments.

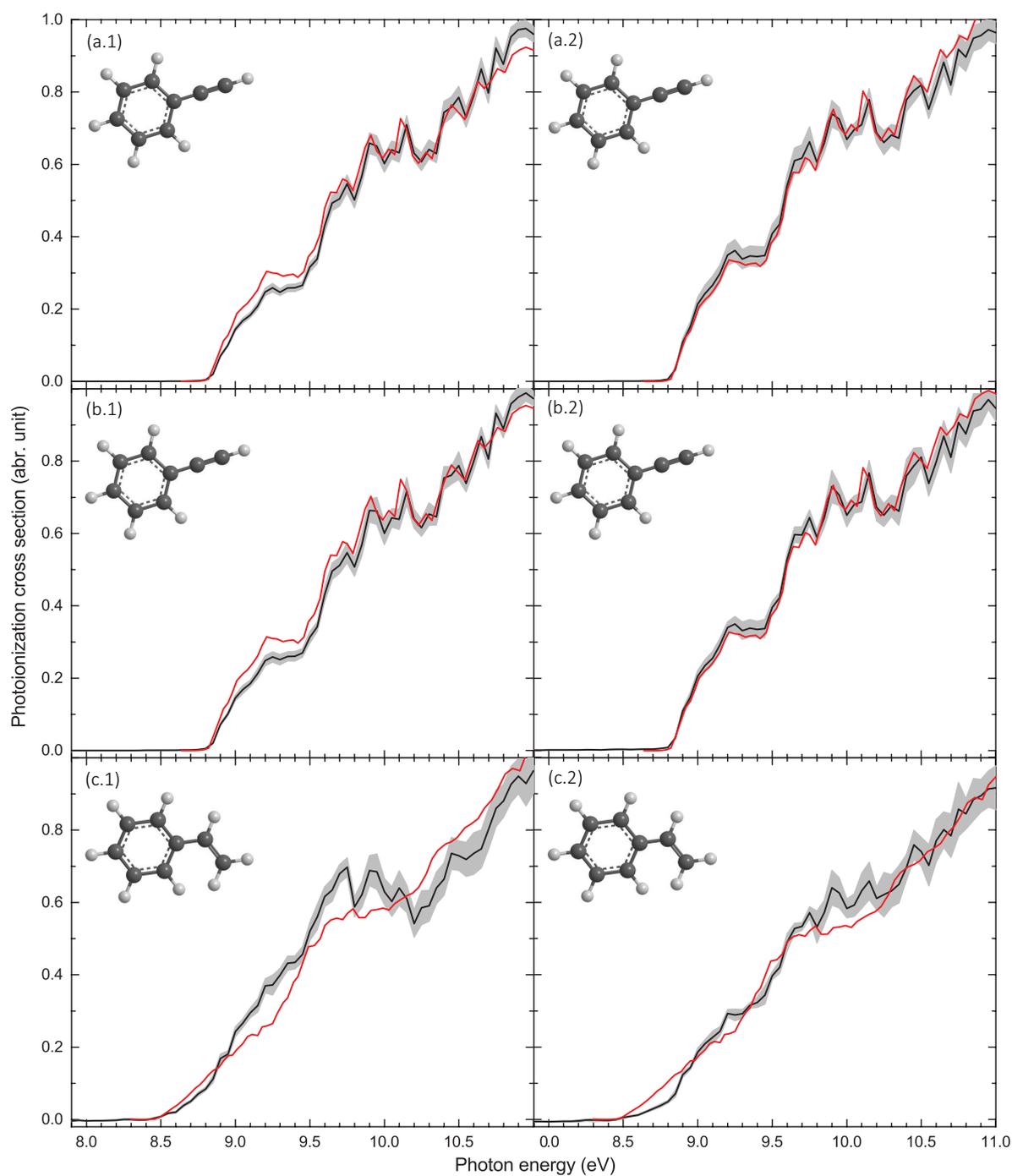


Figure S1. Photoionization efficiency curves recorded at m/z 102 (a.1), 103 (b.1) and 104 (c.1) in the helium-seeded β -bromostyrene system, and those recorded at m/z 102 (a.2), 103 (b.2) and 104 (c.2) in the acetylene-seeded β -bromostyrene system. The black lines show the experimental curves with the errors defined as the gray areas. The red lines indicate the theoretical PIE curves for phenylacetylene^[3] (a), ¹³C-phenylacetylene^[3] (b) and styrene^[3] (c).

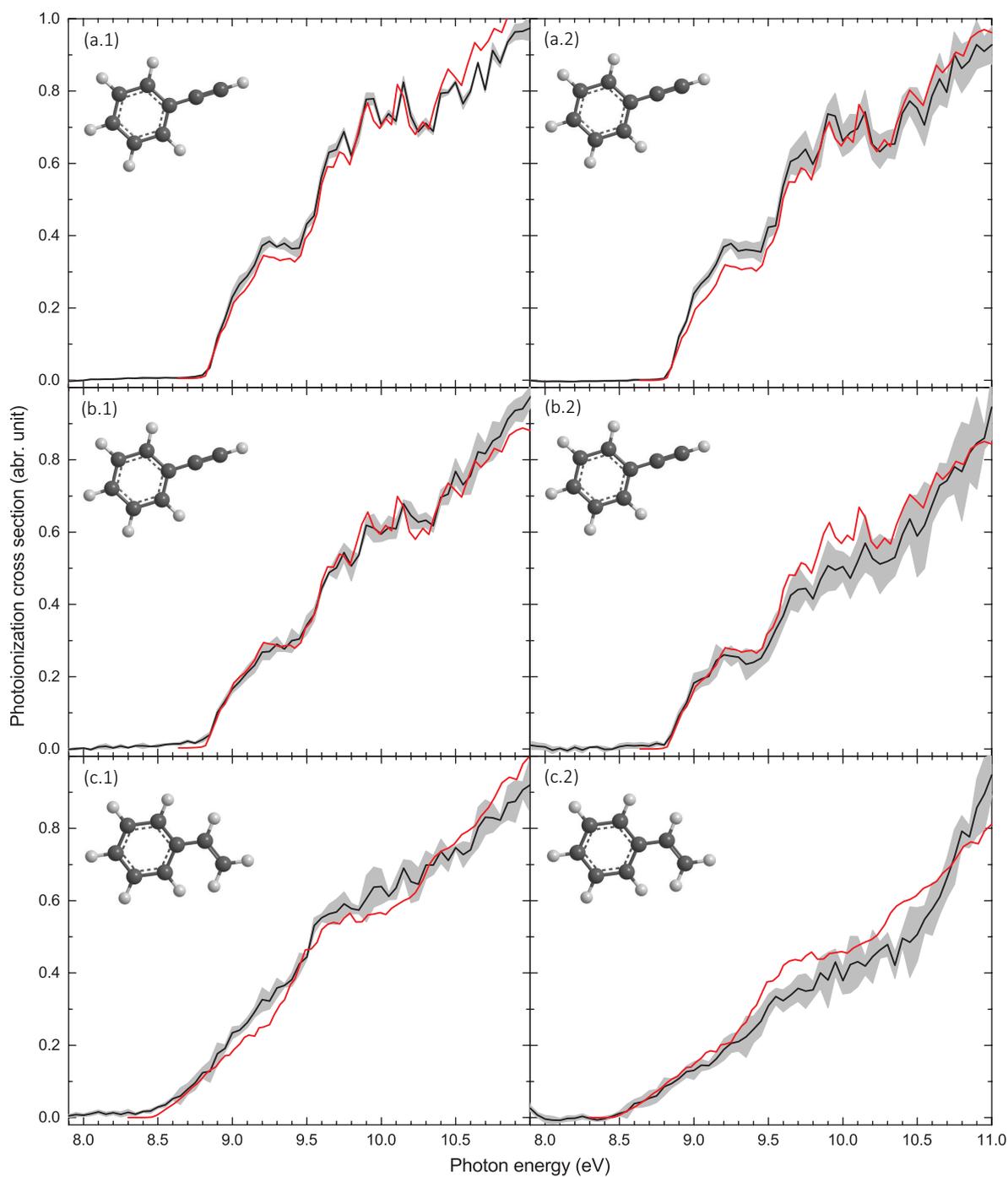


Figure S2. Photoionization efficiency curves recorded at m/z 102 (a.1), 103 (b.1) and 104 (c.1) in the helium-seeded 2-bromostyrene system, and those recorded at m/z 102 (a.2), 103 (b.2) and 104 (c.2) in the acetylene-seeded 2-bromostyrene system. The black lines show the experimental curves with the errors defined as the gray areas. The red lines indicate the theoretical PIE curves for phenylacetylene^[3] (a), ¹³C-phenylacetylene^[3] (b) and styrene^[3] (c).

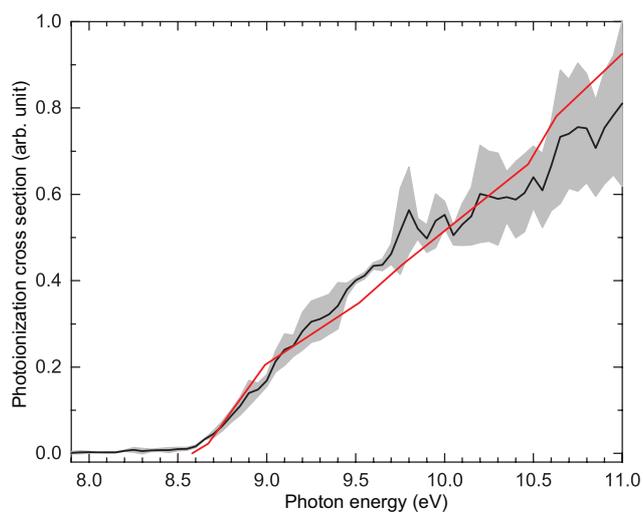


Figure S3. Photoionization efficiency curve recorded at m/z 126 in the acetylene-seeded β -bromostyrene system. The black line shows the experimental curve with the errors defined as the gray area. The red line indicates the theoretical PIE curve for 1,4-diethynylbenzene, which is the only diethynylbenzene isomer available from the database.^[4] However, the experimental PIE may be fitted by the combination of *o*-, *m*-, and *p*-diethynylbenzene isomers.

SI References

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