Electronic Supplementary Information to Formation of phenylacetylene and benzocyclobutadiene in the ortho-benzyne + acetylene reaction

Morgan N. McCabe,[†] Patrick Hemberger,[‡] Dario Campisi,[¶,§] Jeger C. Broxterman,[†] Engelbert Reusch,[‖] Andras Bodi,[‡] and Jordy Bouwman[*,⊥,#,@,△]

†Laboratory for Astrophysics, Leiden Observatory, Leiden University, PO Box 9513, 2300 RA Leiden, The Netherlands

‡Laboratory for Synchrotron Radiation and Femtochemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland

¶Leiden Observatory, Leiden University, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands

§Present address: Chemistry Department, The University of Chicago, 5735 S Ellis Ave, Chicago, IL 60637, USA

‖Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

⊥Laboratory for Astrophysics, Leiden Observatory, Leiden University, PO Box 9513, 2300 RA Leiden, The Netherlands

#Present address: Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80303, USA

@Present address: Department of Chemistry, University of Colorado, Boulder, CO 80309, USA

△Present address: Institute for Modeling Plasma, Atmospheres, and Cosmic Dust (IMPACT), University of Colorado, Boulder, CO 80303, USA

E-mail: jordy.bouwman@colorado.edu

Phone: +31715278432

This Electronic Supplementary Information contains further mass spectra for benzocyclobutenedione, acetylene, and the products of the acetylene + *o*-benzyne reaction at several pyrolysis temperatures as well as further details on the potential energy surface (PES), including transition state geometries and additional calculations performed on the entrance barrier. Furthermore, a zoom in ms-TPE spectrum of **BCBdiene** is shown together with a Franck–Condon simulation. The vibrational normal modes responsible for the **BCBdiene** vibronic progression are also assigned.

A. Benzocyclobutenedione pyrolysis

Figure S1 shows the mass spectrum of the pyrolysis products formed from benzocyclobutenedione (**BCBdione**) (1%) when entrained in argon, at several pyrolysis temperatures and ionized at a photon energy of 10.5 eV. The room temperature mass spectrum shows the presence of two large peaks at m/z 132 and m/z 104, which correspond to **BCBdione** ($C_6H_4(CO)_2$) and $C_6H_4(CO)$, respectively. The formation of the peak at m/z 104 is due to the loss of one of the CO groups and can be attributed to dissociative photoionization at the photon energy of 10.5 eV recorded here.

BCBdione was chosen as a radical precursor as it converts cleanly to *o*-benzyne through double CO loss.[1] As pyrolysis sets in at 996 K, a peak is formed at m/z 76 and is attributed to *o*-benzyne formation by thermal decomposition of **BCBdione** via:

$C_6H_4(CO)_2 \xrightarrow{\Delta T} C_6H_4 + 2\,CO$

Additionally, there are two very small peaks at m/z 77 and m/z 78 which correspond to the ^{13}C isotope of *o*-benzyne along with a small fraction attributed to phenyl radical and benzene, respectively. These species form from *o*-benzyne via hydrogen abstraction reactions:

$C_6H_4 + X{-}H \longrightarrow C_6H_5^{\cdot} + X^{\cdot}$

$C_6H_5^{\cdot} + X{-}H \longrightarrow C_6H_6 + X^{\cdot}$

The depletion of the parent species is complete at temperatures of over 1200 K.

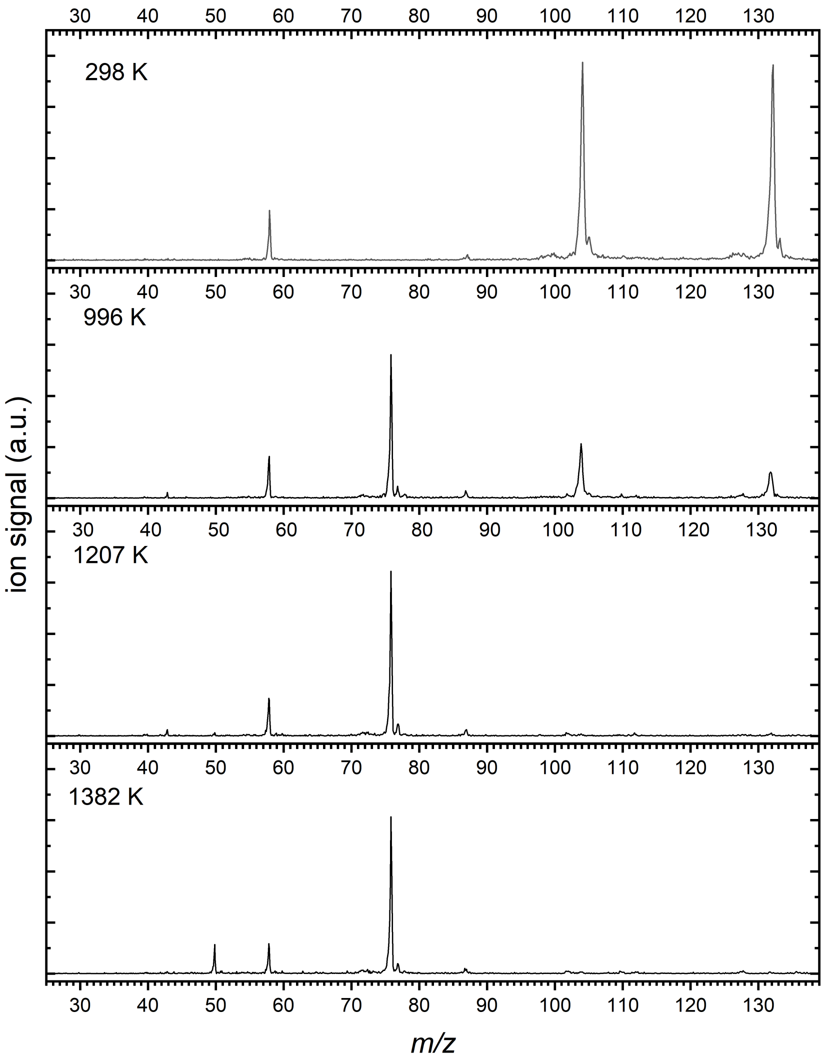


Figure S 1: Mass spectra of 1% **BCBdione** in argon recorded at 10.5 eV and collected at pyrolysis temperatures of 298 K (room temperature), 996 K, 1207 K, and 1382 K.

Temperatures at and exceeding 1380 K show the formation of a peak at m/z 50 formed through pyrolysis of *o*-benzyne via:

$$C_6H_4 \longrightarrow C_4H_2 + C_2H_2$$

This mechanism has previously been reported in high-temperatures *o*-benzyne studies.[1,2]

The peaks at m/z 87 and m/z 110 are contaminants that were present in the detection chamber at the time of measurement. These contaminants do not interfere with the measurements.

B. Acetylene pyrolysis

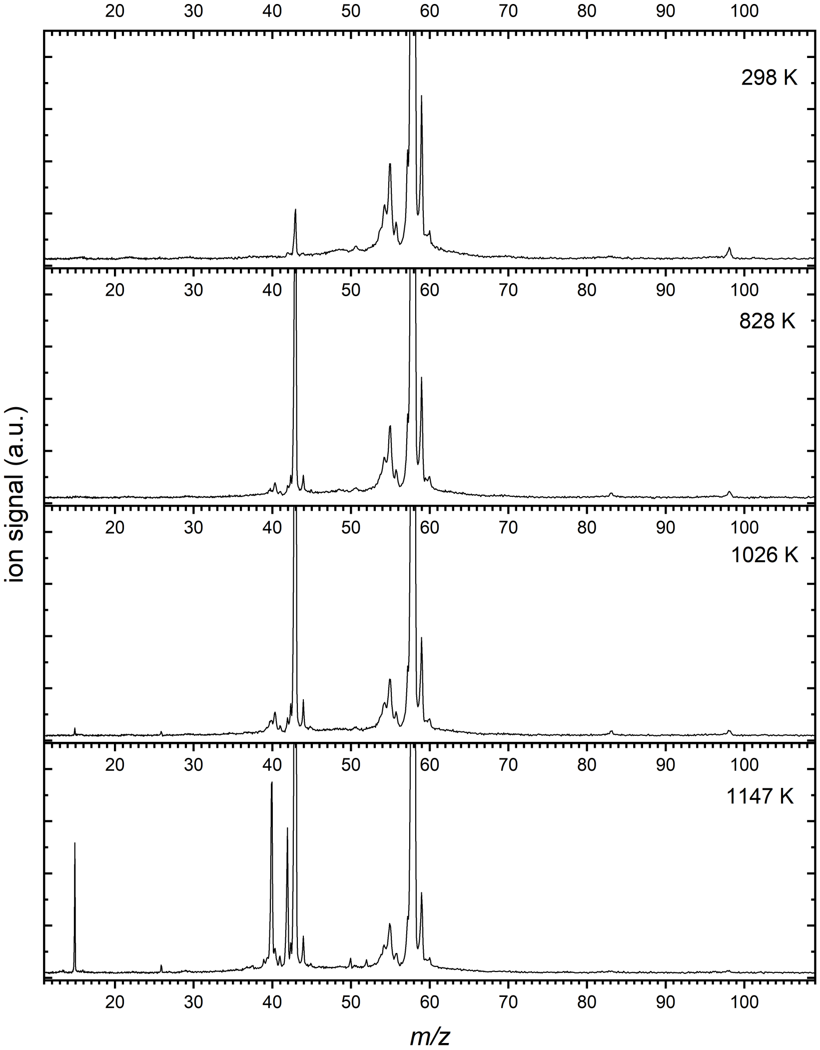


Figure S 2: Mass spectra of neat acetylene recorded at 10.5 eV and at pyrolysis temperatures of 298 K (room temperature), 828 K, 1026 K, and 1147 K.

Figure S2 shows the all-electron mass spectra of acetylene at several pyrolysis temperatures. Notably, there is no peak seen at m/z 26, as the spectra were taken below the ionization energy of 11.4 eV,[3] to prevent saturation of the detector. The large peak present at all pyrolysis temperatures is at m/z 58, and is due to the presence of acetone, added to the acetylene gas cylinder as an inhibitor. At room temperature, there is a small peak at m/z 43 ($CH_3CO^{\cdot}$), which is due to dissociative photoionization of acetone which is known to proceed at photon energies exceeding 10.2 eV[4] via:

$(CH_3)_2CO \xrightarrow{VUV} CH_3CO^+ + CH_3^{\cdot} + e^-$

However, as the pyrolysis temperature is increased it is seen that the signal at m/z 43 is temperature dependent suggesting that thermal decomposition set in via:

$(CH_3)_2CO \xrightarrow{\Delta T} CH_3CO^{\cdot} + CH_3^{\cdot}$,

followed by subsequent ionization of acetyl:

$CH_3CO\cdot \xrightarrow{VUV} CH_3CO^+ + e^-$

This was previously studied in detail and it was concluded that at pyrolysis temperatures below 873 K the acetyl radicals are formed by dissociative ionization rather than thermal dissociation.[4] At pyrolysis temperatures exceeding 1140 K a peak at m/z 15 appears, assigned to methyl radical ($CH_3^{\cdot}$) which stems from the pyrolysis of acetone or further decomposition of acetyl radical:

$CH_3CO^{\cdot} \xrightarrow{\Delta T} CH_3^{\cdot} + CO$

In addition, temperatures above 1147 K show the onset of additional peaks due to pyrolysis. The products and their associated masses are the following: propargyl radical ($C_3H_3^{\cdot}$) at m/z 39, allene/propyne (C_3H_4) at m/z 40, propene (C_3H_6) or ketene (C_2H_2O) at m/z 42. As the methyl signal increases, so too does the signal at m/z 40, indicating that it is likely formed by methyl radical via:

$CH_3^{\cdot} + C_2H_2 \longrightarrow CH_3CHCH^{\cdot} \longrightarrow C_3H_4 + H^{\cdot}$

Additionally, there are small peaks at m/z 50 and m/z 52 previously assigned to diacetylene C_4H_2 and vinylacetylene C_4H_4 via acetylene self reaction in the pyrolysis tube.[4] The small peaks at m/z 83 and m/z 98 are present at room temperature and were confirmed not to be dependent on pyrolysis, and thus do not play a role in the pyrolysis chemistry. Aside from the aforementioned contaminants, no species larger than m/z 58 are seen. Nevertheless, to ensure none of these products interferes with our measurements, temperatures were kept well below 1147 K.

C. Acetylene + *o*-benzyne pyrolysis

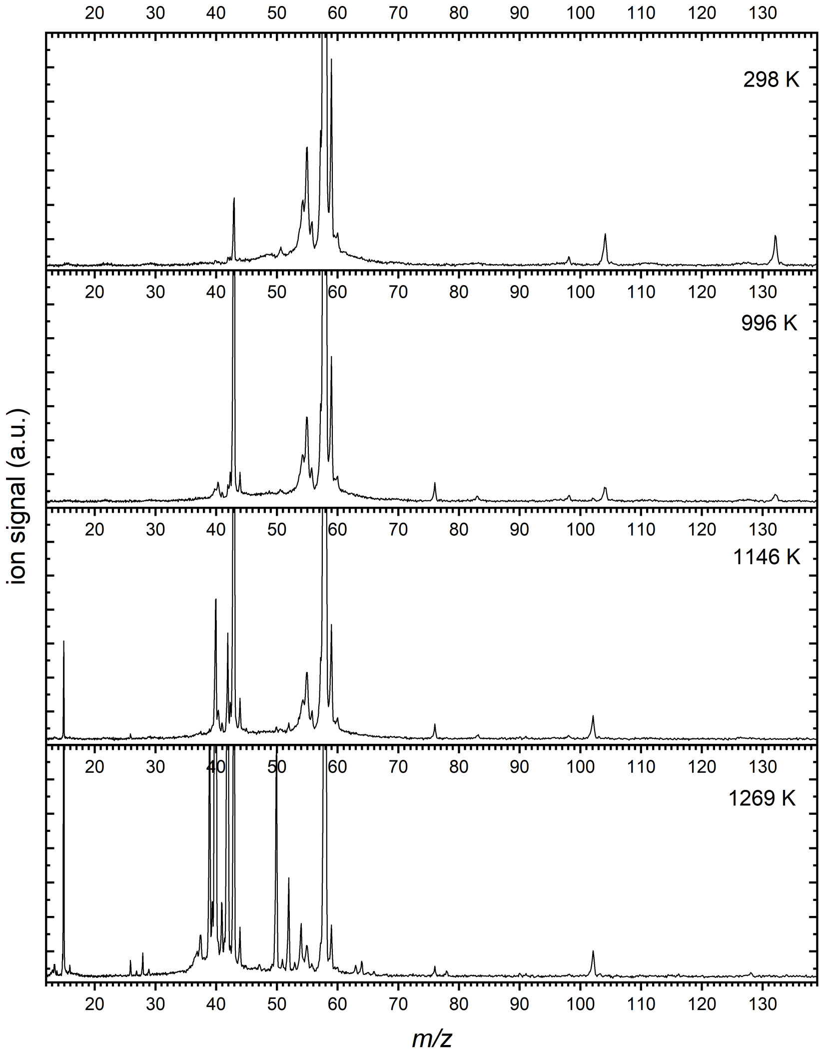


Figure S 3: Mass spectra of 1% **BCBdione** seeded in neat acetylene gas recorded at 10.5 eV and at pyrolysis temperatures of 298 K (room temperature), 996 K, 1146 K, and 1269 K.

Figure S3 shows mass spectra of the reactive mixture after pyrolyzing a mixture of 1% **BCBdione** in acetylene at several microreactor temperatures. As a result, features stemming from both precursors appear in the collected mass spectra. As previously seen at temperatures higher than 1147 K, acetylene side chemistry becomes more prevalent.

Acetone can generate methyl radicals at temperatures above 1100 K. The expected masses for the products formed from the reaction of methyl radical with *o*-benzyne are m/z 90 and

m/z 91 and are not seen in the mass spectra at 1146 K and a very weak sign of these signals grows in at 1269 K. While it is clear that neither acetone nor acetylene side chemistry contributes to the signal at m/z 102, temperatures were kept low (< 1050 K) to minimize side reactions when recording the ms-TPES data of our title reaction.

D. Threshold photoelectron spectrum of BCBdiene

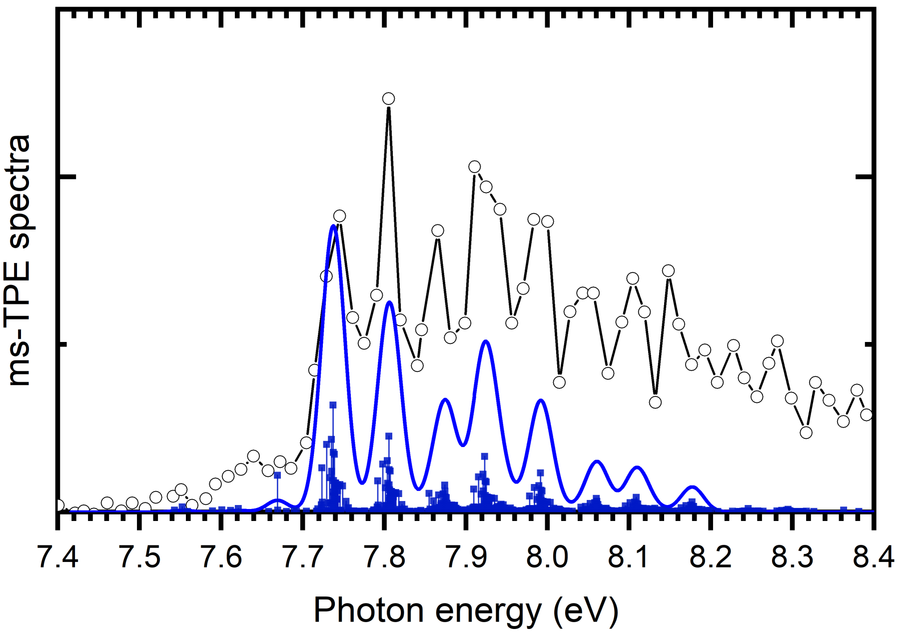
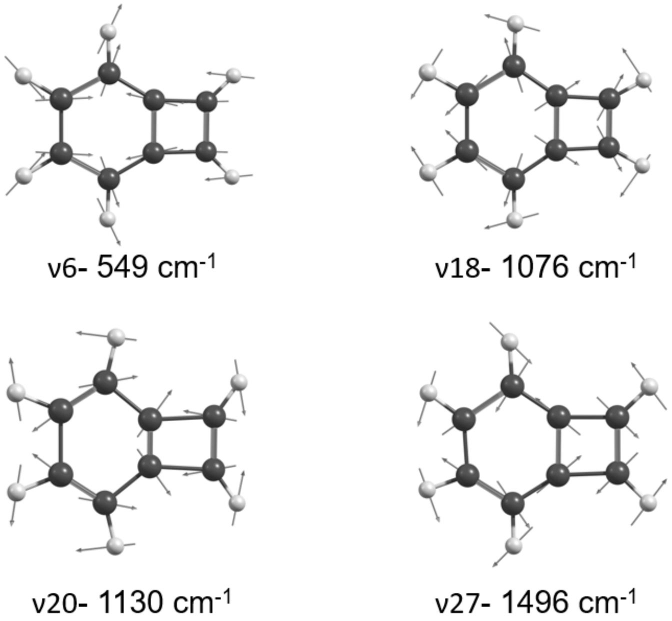


Figure S 4: The threshold photoelectron spectrum of the **BCBdiene** reaction product taken at 1050 K shown together with a Franck–Condon simulation (blue sticks) and a simulated spectrum resulting from the convolution of the stick spectrum with a Gaussian shape with a FWHM of 32 meV.

Figure S4 shows a closer view of the threshold photoelectron spectrum of **BCBdiene** formed from our chemical reaction and shown in Fig. 2 in the main text. Based on Franck–Condon simulations, assignments were made for the vibronic structure. The assigned modes along with the displacement vectors can be seen in Fig. 5. The 0–0 mode is located at 7.74 ± 0.04 eV. The next vibronic band is located at 7.81 eV and is composed largely of transitions involving the ν_6 mode. The next band at 7.87 eV is dominated by simultaneous excitations of two vibrational modes, the ν_{18} and ν_{20} modes. In the cluster around 7.92 eV, most of the intensity is carried by excitations involving the vibrational mode ν_{27}, a mode which is also responsible for the peak at 8.11 eV. Finally, 7.99 eV, 8.06 eV, and 8.19 eV all contain contributions from both ν_6 and ν_{27}.


v6- 549 cm^{-1} v18- 1076 cm^{-1}

v20- 1130 cm^{-1} v27- 1496 cm^{-1}

Figure S 5: The vibrational modes that contribute to the TPES shown in Fig. S4 along with their associated frequencies.

E. Additional Computational Information

Figure S6 shows the transition state geometries of the C_8H_6 PES shown in Fig. 3 of the main text.

Additional calculations were performed for the acetylene + *o*-benzyne reaction using CAS(4,6)/6-311++G(d,p). Applying these calculations to the minimum geometries on the PES, it was found that the energies provided by CAS(4,6) did not match well with those found using the other methods; with energies for closed-shell singlets predicted to be much higher ($>$ 60 kJ/mol) than those resulting from M06-2X and G4 calculations. This was only partly due to the missing size consistency of the calculations.

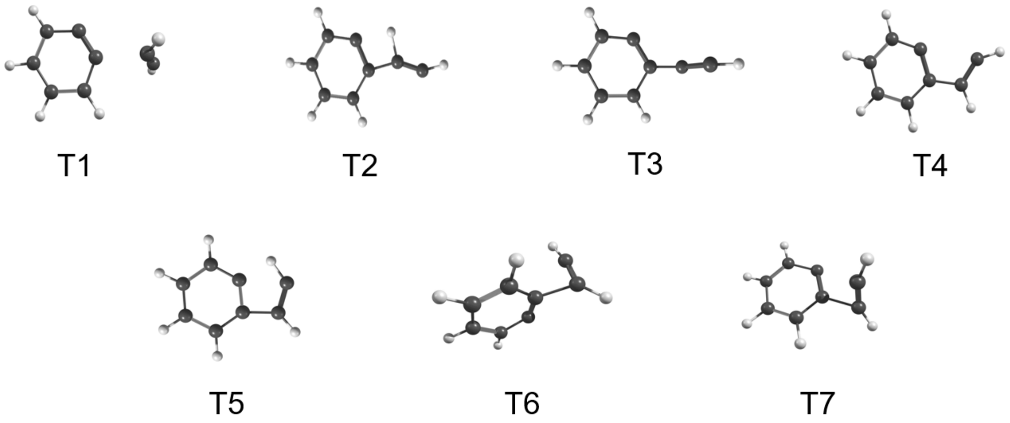


Figure S 6: Transition state geometries on the C_8H_6 potential energy surface reported in the main manuscript

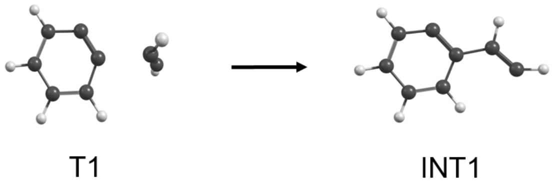


Figure S 7: Geometries of **T1** and **INT1** for the C_8H_6 potential energy surface reported in the main manuscript

While the CAS(4,6) calculations were not conducive in providing more accurate energies for the system, they allowed for further investigation of the entrance channel for the reaction. This pathway was investigated to confirm the geometry change seen on the pathway between **T1** and **INT1**. Specifically, acetylene is seen in **T1** approaching perpendicular to *o*-benzyne, with the initial bond formation causing the acetylene hydrogens to favor a pseudo-trans stereochemistry. However, the formation of the initial OSS intermediate (**INT1**) has the acetylene addition in-plane with *o*-benzyne, with the acetylene hydrogens in a pseudo-cis configuration. From the CAS(4,6) calculations, it was determined that the acetylene is able to rotate freely and that the hydrogen adopting a pseudo-cis/trans geometry had an energy for interconversion below that of the initial entrance barrier.

References

(1) Hirsch, F.; Reusch, E.; Constantinidis, P.; Fischer, I.; Bakels, S.; Rijs, A. M.; Hemberger, P. Self-Reaction of ortho-Benzyne at High Temperatures Investigated by Infrared and Photoelectron Spectroscopy. *J. Phys. Chem. A* **2018**, *122*, 9563–9571.

(2) Zhang, X.; Maccarone, A. T.; Nimlos, M. R.; Kato, S.; Bierbaum, V. M.; Ellison, G. B.; Ruscic, B.; Simmonett, A. C.; Allen, W. D.; Schaefer, H. F. Unimolecular thermal fragmentation of ortho-benzyne. *J. Chem. Phys.* **2007**, *126*, 044312.

(3) Kimura, K.; Katsumata, S.; Achiba, Y. *Handbook of HeI photoelectron spectra of fundamental organic molecules ionization energies, Ab Initio assignments, and valence electronic structure for 200 molecules*; Japan scientific societies Press ; Halsted Press: Tokyo; New York, 1981.

(4) Bouwman, J.; Bodi, A.; Oomens, J.; Hemberger, P. On the Formation of Cyclopentadiene in the C3H5• + C2H2 reaction. *Phys. Chem. Chem. Phys.* **2015**, *17*, 20508–20514.