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Electronic Supplementary Information

On the Formation of Cyclopentadiene in the $C_3H_5\cdot + C_2H_2$ reaction

Jordy Bouwman,* Andras Bodi, Jos Oomens, and Patrick Hemberger

A. Pyrolysis of C_3H_5I in argon

Figure S1 shows the all-electron pyrolysis mass spectra of allyl iodide in argon at a temperature of 833 K and photon energies of 9.5 eV and 10.5 eV. The bottom trace of Figure S1 shows that allyl iodide ($m/z = 168$) is efficiently converted into the allyl radical ($m/z = 41$) and atomic iodine. In accordance with Fischer et al.,¹ the top panel and its inset in Figure S1 show that some of the formed allyl is converted into allene or propyne ($m/z = 40$) by hydrogen abstraction and some of the allyl is converted into propargyl ($m/z = 39$) + H_2 by dissociative ionization at 10.5 eV. Iodine atoms and HI are detected at 10.5 eV and point to hydrogen abstraction reactions by I atoms. Alternatively, HI can be formed by a direct elimination from allyl iodide. Molecular iodine is also formed and detected at $m/z = 254$. An overview of ionization energies relevant to the pyrolysis experiments described in this work is given in Table S1.

Table S1: Ionization energies in eV of species relevant to the pyrolysis experiments reported here taken from NIST.²

Name	Structure	m/z	I.E.	Name	Structure	m/z	I.E.
Allyliodide	C ₃ H ₅ I	168	9.27	1,5-hexadiene	C ₆ H ₁₀	82	9.29
Acetylene	C ₂ H ₂	26	11.4	Iodine	I ₂	254	9.31
Acetone	(CH ₃) ₂ CO	58	9.70	Acetyl	C ₂ H ₃ O	43	8.05
Propene	C ₃ H ₆	42	9.73	Allyl	C ₃ H ₅	41	8.18
Allene	C ₃ H ₄	40	9.69	Vinyl	C ₂ H ₃	27	8.25
Propyne	C ₃ H ₄	40	10.37	Iodine atom	I	127	10.45
Methyl	CH ₃	15	9.84	Hydrogeniodide	HI	128	10.39
Ketene	C ₂ H ₂ O	42	9.62	Diacetylene	C ₄ H ₂	50	10.17
Vinylacetylene	C ₄ H ₄	52	9.58	Propargyl	C ₃ H ₃	39	8.67
Ethene	C ₂ H ₄	28	10.51				

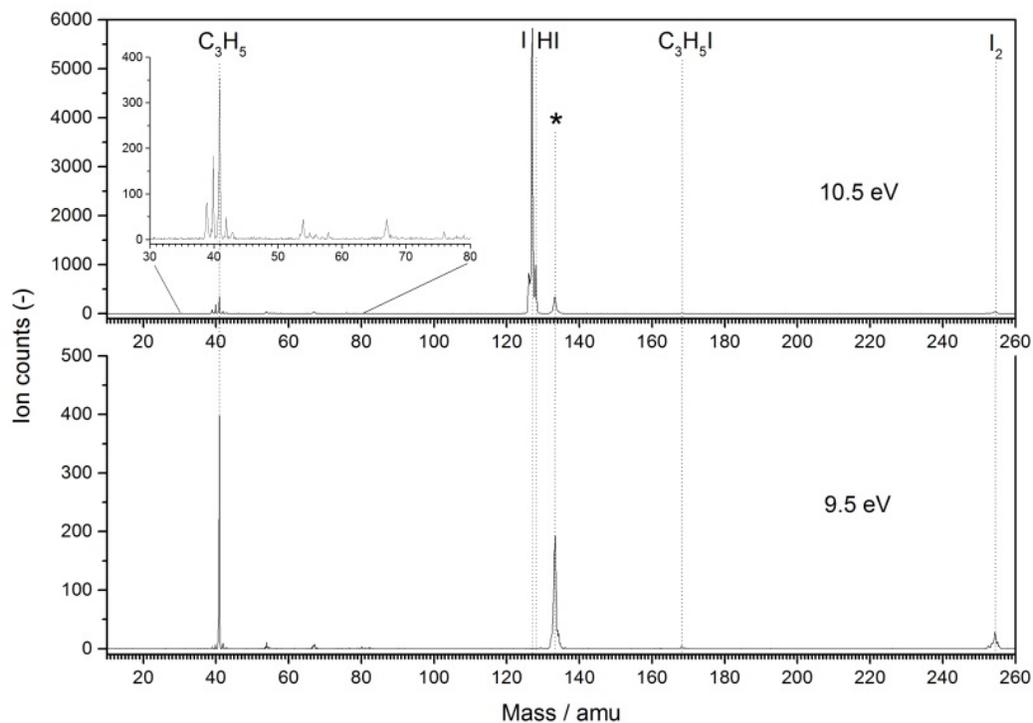


Figure S1: All-electron mass spectra of the pyrolysis of 0.5% allyl iodide in argon recorded at 833 K and at a photon energy of 9.5 eV (bottom) and 10.5 eV (top). The inset shows a blow-up of the top trace. Note: the peak marked with an asterisk (*) is caused by a 1,2,3,4-

tetrahydroquinoline ($m/z = 133$) contamination in the detection chamber, of which neither the parent nor the fragment ions interfere with the measurements reported here.

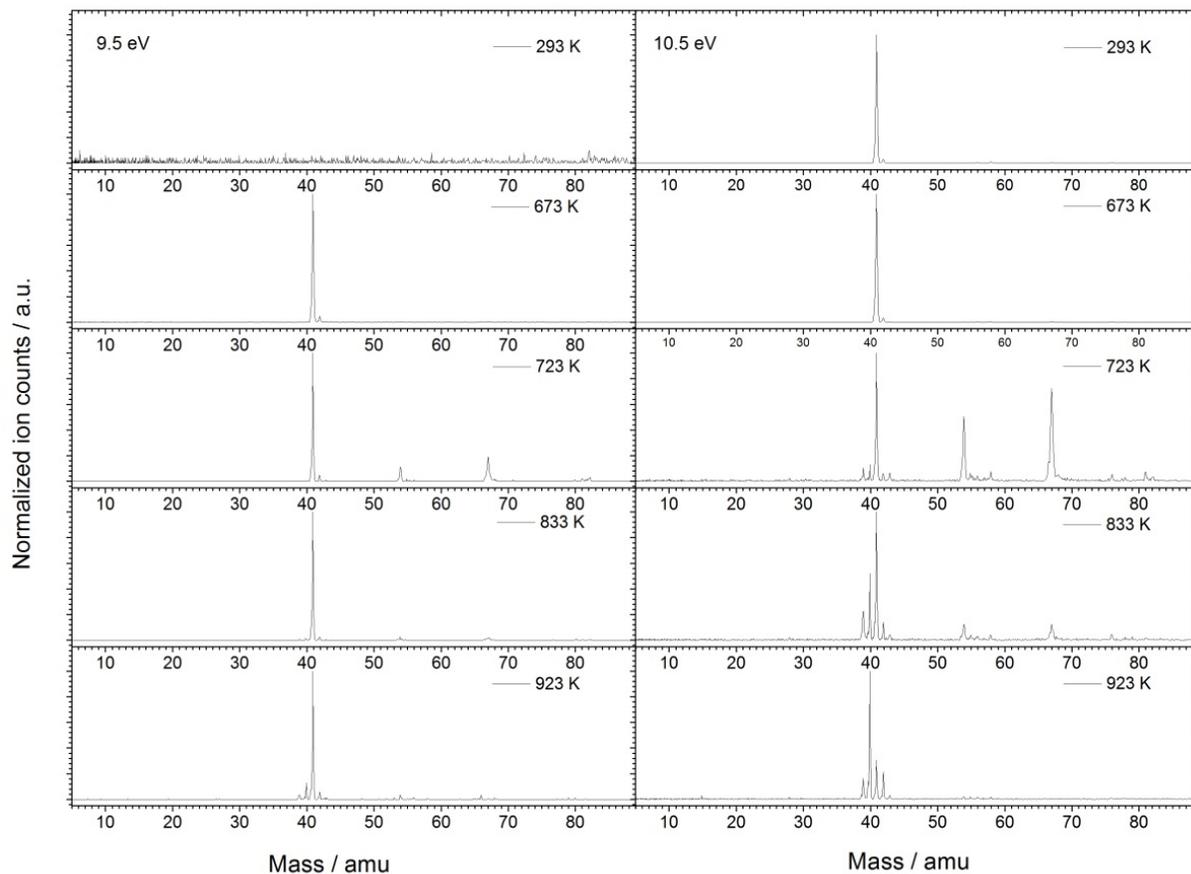
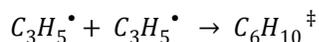


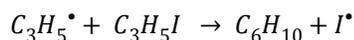
Figure S2: All-electron mass spectra recorded for pyrolysis of C_3H_5I in Ar at temperatures of 293, 673, 723 K, 833 K, and 923 K at photon energies of 9.5 eV (left column) and 10.5 eV (right column). All mass spectra are normalized to the strongest signal.

The temperature dependence of the all-electron mass spectra, normalized to the strongest peak recorded for pyrolysis of C_3H_5I in argon for masses spanning $m/z = 5$ to 87 is shown in Figure S2. Chemical reactions occur in the pyrolysis tube in absence of the reactant gas, acetylene, as is seen from the rising signal at $m/z = 54$ and $m/z = 67$ at temperatures above 700 K. Furthermore, a very small signal is detected at $m/z = 82$ in the spectra recorded at 723 K. The corresponding peak intensities decrease as the temperature is further increased. Fischer et al.¹ also identified the peaks at $m/z = 54$ and 67 in the pyrolysis of C_3H_5I , as well as in the ionization

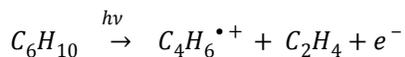
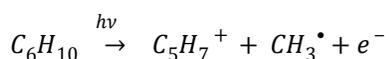
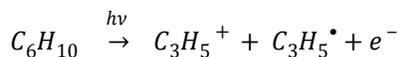
of diallyl at 10.5 eV at room temperature. From this observation they concluded that a reaction between allyl radicals forms 1,5-hexadiene (diallyl):



In the absence of third body collisions in the reactor, the reverse reaction is expected to deplete the diallyl population quantitatively. Hence, we propose that the reaction between C_3H_5I and allyl forms diallyl via I-elimination, which allows for excess energy release and the stabilization of the diallyl species, which is detected in small quantities at $m/z = 82$:



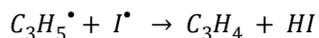
Diallyl has an unstable parent ion and almost always undergoes dissociative ionization, which explains the low intensity of the $m/z = 82$ peak as compared with that of the products:



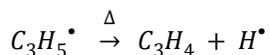
The first channel, the formation of the allyl cation by dissociative ionization of diallyl, requires a much higher photon energy of 11.25 eV¹ compared with the 9.35 eV appearance energy of $C_5H_7^+$,³ and is thus expected to be a minor channel at all energies and does not contribute to the allyl ion signal in our mass spectra.

As seen in Figure S2, the signals at $m/z = 54$ and 67 reach a maximum at 723 K. The fact that the contributions of these ions becomes smaller as the temperature increases can be

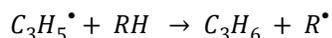
attributed to a lowering of the allyl density with increasing temperature, which may be due to several factors. First, as described by Fischer et al.,¹ allyl radicals undergo hydrogen abstraction by I-atoms yielding allene and (also detected) HI:



Second, allyl radicals can undergo thermal decomposition, giving rise to allene or propyne:



Both paths support the observation that as the temperature increases a larger contribution of $m/z = 40$ (C_3H_4) is observed at the expense of the allyl peak. The absence of the $m/z = 40$ peak when using 1,5-hexadiene as a precursor, however, led Fischer et al. to rule out the H-abstraction path. A small signal observed at $m/z = 42$ points to another allyl loss channel. This is likely propene that is formed via hydrogen abstraction by allyl from a hydrocarbon, RH, in the reactor:



Further, the signal recorded at $m/z = 39$ is attributed to either the cyclopropenyl cation or the propargyl cation. Fischer et al. proposed that this species is formed via dissociative ionization of allyl. At a photon energy of 9.5 eV, however, a weak C_3H_3 signal is observed at 923 K (Figure S2). At a photon energy of 10.5 eV, the signal grows in at 723 K. This observation suggests that C_3H_3 could be formed via thermal dissociation *as well as* dissociative ionization of thermally activated allyl.

B. Pyrolysis of acetylene (containing traces acetone)

Acetylene pyrolysis products have been measured for a set of temperatures and photon energies to be able to distinguish between acetylene chemistry and allyl + acetylene chemistry. Traces of acetone are present in all the acetylene pyrolysis experiments, because it is used as a stabilizing agent and makes up ~0.5% of the gas that is taken from the cylinder.

The all-electron mass spectra recorded of the pyrolysis of acetylene are shown in Figure S3. The peak at $m/z = 58$ corresponds to the acetone radical cation ($C_3H_6O^+$) and the temperature dependent signal that grows in at $m/z = 43$ corresponds to the acetyl cation ($C_2H_3O^+$). Dissociative photoionization of acetone by methyl loss yielding CH_3CO^+ sets in at around 10.2 eV in a room temperature sample,⁴ but at 573 K, CH_3CO^+ is already detected at 9.5 eV, opening the possibility that thermal dissociation of acetone occurs. In dissociative photoionization, only the fragment with the lower ionization energy will be charged, whereas in thermal dissociation both fragments can be ionized by VUV radiation. However, we have to increase the photon energy above the IP of the methyl radical, 9.84 eV (Table S1), in order to differentiate between dissociative photoionization and thermolysis. At 10.5 eV both the methyl radical as well as the acetyl radical can be ionized. At this photon energy, the methyl radical is not observed below 873 K, and even at 873 K the ratio between methyl radical and acetyl signal is ~1:100. While this fraction also reflects the difference in VUV absorption cross section of the two species, it is mostly determined by difference in relative abundance. The methyl radical ionization cross section is 6 MB, $6 \cdot 10^{-22} \text{ m}^2$, at 10.5 eV,⁵ whereas the acetyl radical ionization cross section is estimated at 18 MB by the method developed by Bobeldijk et al.⁶ Hence, after correction for the cross section, the abundance of methyl radicals at 873 K is lower by a factor of ~33 than the fraction of acetyl radicals. Hence, we conclude that acetone is stable at and below a reactor

temperature of 873 K and its fragments are due to dissociative ionization, rather than thermal dissociation.⁷ The fact that dissociative ionization also occurs at 9.5 eV, i.e. 0.7 eV below the room temperature appearance energy, is caused by the fact that the thermal energy distribution of the neutral is shifted into the ion manifold, resulting in a red-shift of the onset for dissociative ionization.^{8,9} Thus, the thermal decomposition of acetone only seems to play a significant role at temperatures exceeding 873 K.

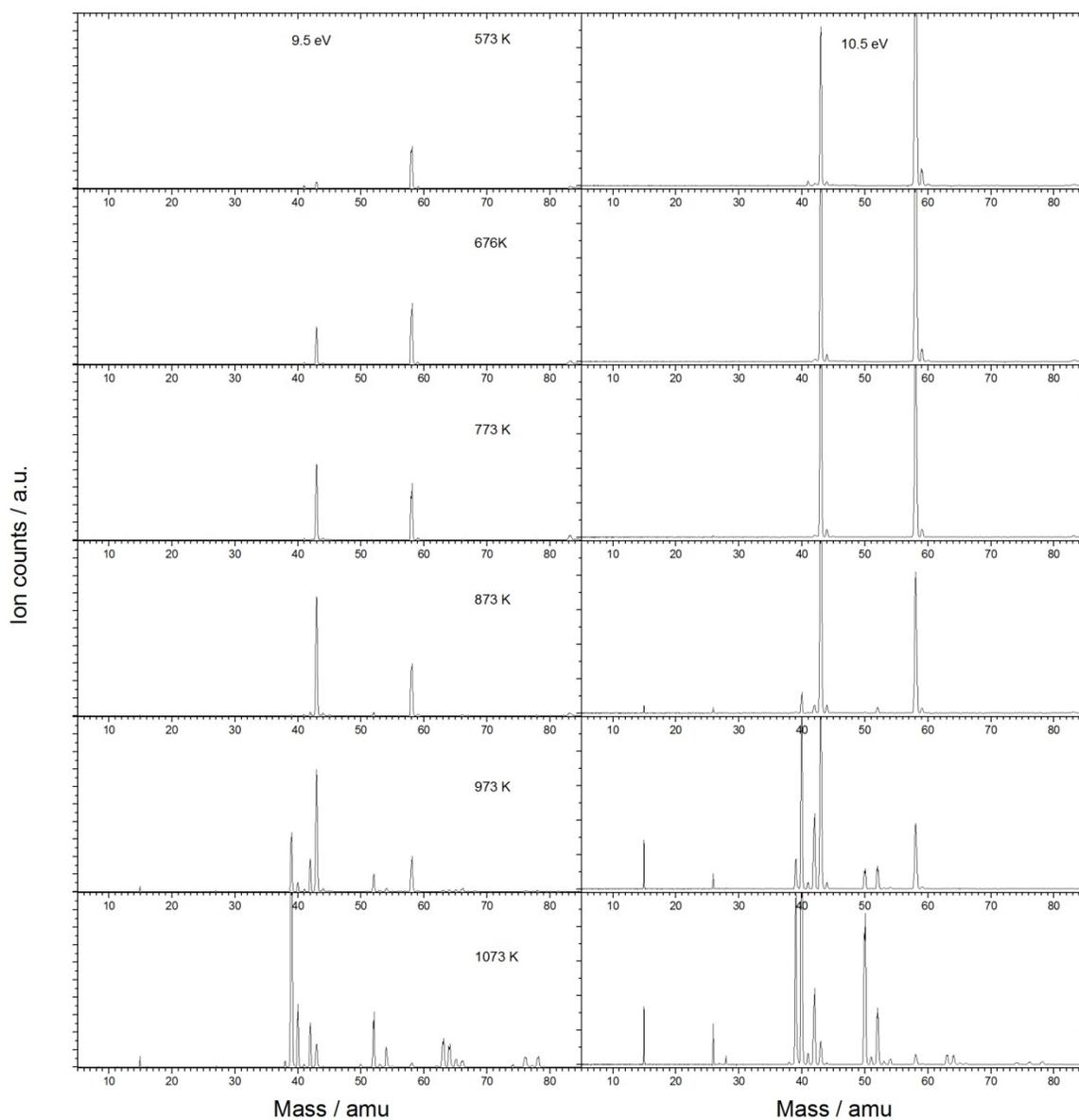


Figure S3: All-electron mass spectra recorded for the pyrolysis of acetylene with traces of acetone, recorded at a photon energy of 9.5 eV (left) and 10.5 eV (right), and at temperatures of 573, 676, 773, 873, 973, and 1073 K.

More pyrolysis products are detected when the temperature exceeds 873 K and acetylene also participates in the chemistry. Most notably, products are detected at $m/z = 39$, 40, 42, 50 and 52. These can be assigned as follows: $m/z = 39$ corresponds to the propargyl radical ($C_3H_3^*$), $m/z = 40$ is due to allene or propyne (C_3H_4), and $m/z = 42$ can be ascribed to either propene (C_3H_6),

or to ketene (C₂H₂O). The latter can be formed in the thermal decomposition of acetone or the acetyl radical.^{4,10} Pure acetylene pyrolysis yields species with an even number of carbon atoms.¹¹ Odd numbered carbon species are detected because acetone or acetone fragments participate in the chemistry. The peaks at $m/z = 50$ and 52 are ascribed to diacetylene (C₄H₂) and vinylacetylene (C₄H₄), respectively, which are formed through acetylene self-reactions in the pyrolysis tube.¹² An assignment of the origin of these species is beyond the scope of this manuscript and we only need to be aware of these products in the analysis of products from the allyl + acetylene reaction.

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