

View Article Online View Journal

# PCCP

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: F. Holzmeier, I. Fischer, B. Kiendl, A. Krueger, A. Bodi and P. Hemberger, *Phys. Chem. Chem. Phys.*, 2016, DOI: 10.1039/C6CP01068G.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/pccp

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42.

# YAL SOCIETY CHEMISTRY

### Phys. Chem. Chem. Phys.

## ARTICLE

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

On the Absolute Photoionization Cross Section and Dissociative Photoionization of Cyclopropenylidene

Fabian Holzmeier,<sup>a</sup> Ingo Fischer,<sup>\*,a</sup> Benjamin Kiendl,<sup>b</sup> Anke Krueger,<sup>b</sup> Andras Bodi,<sup>c</sup> and Patrick Hemberger\*,c

We report the determination of the absolute photoionization cross section of cyclopropenvlidene.  $c-C_3H_2$  and the heat of formation of the C<sub>3</sub>H radical and ion derived by the dissociative ionization of the carbene. Vacuum ultraviolet (VUV) synchrotron radiation as provided by the Swiss Light Source and imaging photoelectron photoion coincidence (iPEPICO) were employed. Cyclopropenylidene was generated by pyrolysis of a quadricyclane precursor in a 1:1 ratio with benzene, which enabled us to derive the carbene's near threshold absolute photoionization cross section from the photoionization yield of the two pyrolysis products and the known cross section of benzene. The cross section at 9.5 eV, for example, was determined to be 4.5±1.4 Mb. Upon dissociative ionization the carbene decomposes by hydrogen atom loss to the linear isomer of  $C_3H^+$ . The appearance energy for this process was determined to be  $AE_{0K}(c-C_3H_2; l-C_3H^+)=13.67\pm0.10 \text{ eV}$ . The heat of formation of neutral and cationic C<sub>3</sub>H was derived from this value via a thermochemical cycle as  $\Delta_{i}H_{OK}(C_{3}H) = 725 \pm 10^{-10}$ 25 kJ mol<sup>-1</sup> and  $\Delta_r H_{nk}(C_3 H^+) = 1604 \pm 19$  kJ mol<sup>-1</sup>, using a previously reported ionization energy of C<sub>3</sub>H.

#### 1. Introduction

In this paper we report the absolute photoionization cross section of cyclopropenylidene, c-C<sub>3</sub>H<sub>2</sub>, near its ionization threshold. In addition, we investigated the dissociative photoionization (DPI) of the carbene employing imaging photoelectron photoion coincidence spectroscopy (iPEPICO) with VUV synchrotron radiation.

Along with its isomer propargylene, cyclopropenylidene was identified in a rich cyclopentene flame by photoionization mass spectrometry (PIMS),<sup>1</sup> based on its ionization energy (IE) of 9.17 eV as determined by conventional<sup>2-4</sup> and threshold photoelectron spectroscopy (TPES).<sup>5</sup> Furthermore, it is assumed to dominate the dissociation dynamics of the resonantly stabilized propargyl radical at low combustion temperatures or low pressures.<sup>6</sup> For a deeper insight into flame chemistry, reaction rates are of great interest. These can be extracted from PIMS experiments if the absolute concentrations of all reactants in the flame can be determined.7, 8 Therefore, it is necessary that the absolute photoionization cross section  $\sigma_i$  of each of the involved species is known to relate the observed ion signal to the

concentration. Due to their importance in kinetics and analytical chemistry, the cross sections of numerous species relevant in hydrocarbon combustion processes have already been determined.<sup>9, 10</sup> Absolute photoionization cross sections are usually extracted by comparing the photoion yield of the two components of a binary mixture with a defined stoichiometry, from which the cross section of one component is exactly known. While such mixtures can be easily prepared for stable molecules, the determination of photoionization cross sections for unstable molecules, e.g. radicals and carbenes, is challenging. Subsequently,  $\sigma_i$  is known for only few reactive open-shell species, vinyl,<sup>11</sup> propargyl,<sup>11-13</sup> allyl,<sup>14</sup> 2-propenyl,<sup>14</sup> phenyl,<sup>15</sup> methyl,<sup>16, 17</sup> and ethyl<sup>18</sup> among them.

Here we employ the strategy of producing a reactive molecule together with a well-studied stable molecule from a joint precursor. Cyclopropenylidene can be generated by pyrolysis of a quadricyclane derivative (see Fig. 1),<sup>19, 20</sup> and benzene is generated as a second pyrolysis product. The latter's absolute photoionization cross section has been determined previously<sup>10, 21</sup> and it has an IE similar to cyclopropenylidene.<sup>22</sup> As both pyrolysis products are generated in a 1:1 ratio, it is possible to determine the absolute photoionization cross section of cyclopropenylidene by comparing the photoionization efficiency (PIE) curves of  $c-C_3H_2$  and benzene.

In a second experiment, the dissociative photoionization of cyclopropenylidene was investigated and an H-loss appearance energy determined. Recording and analysing the breakdown diagram of unstable intermediates can potentially yield valuable thermochemical data, but has proved to be rather challenging. Selected data were obtained for the allyl,<sup>23, 24</sup> propargyl,25 and ethyl radicals,25 but no full breakdown

<sup>&</sup>lt;sup>a.</sup> Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany.

<sup>&</sup>lt;sup>b.</sup> Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany. <sup>c</sup> VUV Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.

<sup>\*</sup> Email: ingo.fischer@uni-wuerzburg.de, patrick.hemberger@psi.ch.

Electronic Supplementary Information (ESI) available: [details of

any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C6CP01068G Phys. Chem. Chem. Phys.

#### ARTICLE

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42.

diagram of a polyatomic reactive intermediate has been reported yet to the best of our knowledge. The generally low signal levels, overlapping peaks from the dissociative photoionization of the precursor and the radical intermediate, and broad internal energy distributions because of the increased temperature complicated measurements. A further difficulty is the spin state of the parent and daughter ions. Open-shell radicals yield stable, closed-shell parent ions, which typically dissociate into two open-shell fragments or two closed-shell ones over a non-negligible reverse barrier.24, 25 Since cyclopropenylidene is a singlet carbene, it is a prime candidate to circumvent this issue, as the cation should fragment into an open-shell and a stabilized closed-shell species. A second observation is that even in the few cases with experimental data on the breakdown diagram for a pyrolysis product, the deduced internal energy distribution corresponded to a much higher temperature than the experimental one.<sup>24, 26</sup> This is at odds with Franck-Condon simulations of the hot bands in the more readily available threshold photoelectron spectra of the species, which typically shows a lower and more realistic temperature. As will be shown below, the cyclopropenylidene breakdown diagram is also affected, and we identify three possible underlying Dissociative reasons and discuss their likelihood. photoionization yields access to validated thermochemical information. In addition, as dissociative photoionization processes take place on the same potential energy surface as ion-molecule reactions, and each dissociation corresponds to the inverse of an association reaction,<sup>27</sup> breakdown diagrams may also be relevant from an astrochemical point of view, as cations are abundantly formed and found in space.<sup>28</sup> Cyclopropenylidene is indeed one of the most abundant hydrocarbons in interstellar space and appears with significant concentration in diffuse interstellar clouds.<sup>29-34</sup> The high intensity of high-energy electromagnetic radiation in the interstellar medium leads to molecular ions and therefore, ionmolecule reactions dominate interstellar chemistry due to their long range potential and often negligible barriers.<sup>35-39</sup> The cationic potential energy surface of  $C_3H_2^+$  has been explored for this reason.<sup>36, 40</sup> Investigating the DPI of cyclopropenylidene sheds light onto bonding properties of the  $c-C_3H_2^+$  cation and will provide access to the thermochemistry of daughter ions, thus leading to a better understanding of interstellar chemistry. Since  $c-C_3H_2$  is the most abundant cyclic hydrocarbon in the interstellar space, the presence of energetic radiation may lead to other fragments, e.g.,  $I-C_3H^+$ , which has been observed in the Horsehead photodissociation  $\mathsf{region}^{41}$  and toward Sgr B2(N).  $^{42,\,43}$ 

These two experiments complete a series of investigations on the cyclopropenylidene carbene in our group, in which we analysed the near-threshold photoionization by threshold photoelectron spectroscopy (TPES),<sup>5</sup> investigated the photophysics and photochemistry of the <sup>1</sup>B<sub>1</sub> excited state by multiphoton ionization, Doppler spectroscopy,<sup>44</sup> femtosecond time-resolved photoionization and photoelectron spectroscopy,<sup>45</sup> and studied the photodissociation dynamics by photofragment velocity map imaging.<sup>20</sup>

#### 2. Experimental

The experiments were performed at the VUV X04DB beamline at the Swiss Light Source (SLS) storage ring utilizing the iPEPICO (imaging photoelectron photoion coincidence) endstation. Details on the beamline optics<sup>46</sup> and the iPEPICO setup<sup>47, 48</sup> can be found in the literature and are thus only briefly described here. Vacuum ultraviolet (VUV) synchrotron radiation is provided by a bending magnet and collimated onto a grazing incidence monochromator equipped with a 150 lines/mm plane grating. The photon energy resolution is approximately  $E/\Delta E = 10^3$ . The monochromatic radiation is focused into a rare gas filter operated with a mixture of Ne/Ar/Kr (7 eV < hv < 14 eV) or pure Ne (11 eV < hv < 21 eV) to suppress higher harmonic radiation and is then passed to the endstation, where it crosses the sample molecular beam.

The precursor molecule, a quadricyclane depicted in Fig. 1, was synthesized according to the route described in Ref.<sup>20</sup>. The liquid was held at 15°C to prevent decomposition, seeded in 1.8 bar of argon and expanded into the experimental chamber through a 100 µm orifice passing a SiC tube electrically heated to 740 K as measured by a Type C thermocouple. Details on the pyrolysis source can be found elsewhere.<sup>49</sup> The pyrolysis products were then ionized by VUV radiation and detected in the iPEPICO spectrometer. Electrons and ions are extracted by a 120 V cm<sup>-1</sup> electric field and the electrons are velocity map imaged onto a position sensitive delay line anode (Roentdek DLD40), while the ions are detected in coincidence in a Wiley-McLaren time-of-flight (TOF) mass spectrometer. The photon energy was calibrated on the 11s', 12s', and 13s' autoionization resonances of Ar in first and second order. Mass-selected threshold photoelectron (ms-TPE) spectra were extracted by selecting the central part of the photoelectron image corresponding to electrons with a kinetic energy of less than 5 meV which were followed by an ion event in the corresponding time-of-flight range. Hot electron contribution was subtracted as proposed by Sztáray and Baer.<sup>50</sup> The photoion yield (PIY) was obtained by summing all electron signal detected in coincidence with the selected mass range and the signal was normalized to the photon flux as measured by a SXUV-100 photodiode from IRD, taking into account the energy dependent response. Due to the limited size of the electron image, only electrons with a kinetic energy below about 1 eV are completely imaged onto the detector. The electron signal was accumulated for 6 min in steps of 10 meV for the low energy spectra presented in this paper, while the step size and the acquisition time were increased to 50 meV and 8.5 min, respectively, for the high energy spectra.

Unless stated otherwise, energy computations were performed on CBS-QB3 level of theory,<sup>51, 52</sup> utilizing the Gaussian09 suite of programs.<sup>53</sup> Ionization energies were obtained by subtracting the neutrals' energy from the cations' one and appearance energies are derived from the difference of the product energies (daughter ion + neutral fragment) and the parent's energy, if there is no reverse barrier. Scans of the reaction coordinates for the localization of transition states were performed on B3LYP/6-31G(d) and CASSCF-

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42.

#### Journal Name

MP2(7,10)/cc-pVTZ level of theory. Franck-Condon simulations including hot band contribution were conducted with the program ezSpectrum<sup>54</sup> and the program MinimalPEPICO<sup>55</sup> was used to fit the breakdown diagram of cyclopropenylidene.

#### 3. Results and Discussion

#### 3.1 Photoionization Cross Section

As visible in the mass spectrum given in Fig. 1 and shown previously,<sup>19, 20</sup> the quadricyclane derivative (m/z=116) yields cyclopropenylidene,  $c-C_3H_2$ , and benzene upon pyrolysis with a high conversion efficiency. The only observed dissociative photoionization channel of the precursor is associated with Hatom loss and is responsible for the peak at m/z=115. A further peak at m/z=109 is due to 3-methoxypyridine, which was studied previously and does not interfere with the present experiment.<sup>63</sup> Benzene has a similar ionization energy as cyclopropenylidene and its absolute photoionization cross section is available from previous works.<sup>10, 21</sup> As m/z = 38 and m/z = 78 are the only relevant fragments generated upon pyrolysis of the quadricyclane precursor,  $c-C_3H_2$  and benzene must be generated in a stoichiometric quantity. Other species (m/z = 39, 40 and 66) are only present in minuscule amounts, originate from a previous experiment, and are therefore neglected. The mass-selected threshold photoelectron (ms-TPE) spectra corresponding to these two mass peaks were hence recorded to check if the observed signals can indeed be assigned to cyclopropenylidene and benzene or if other isomers also contribute to the mass peaks. As expected, the ms-TPE spectrum corresponding to m/z = 78 (not shown in this paper) represents a perfect match with previously reported spectra of benzene confirming an IE of 9.24 eV.<sup>22</sup> The ms-TPE spectrum corresponding to m/z=38 is shown in Fig. 2. It matches the earlier TPE spectrum of cyclopropenylidene obtained utilizing the 1-chlorocycloprop-2-ene precursor<sup>5</sup> and confirms the previously reported ionization energy of 9.17 eV for  $c-C_3H_2$ . The signal/noise ratio is significantly improved in the new spectrum and the observed vibrational structure confirms the previous assignment of vibrational bands. A pronounced band at 9.02 eV was observed in the TPE spectrum of Hemberger et al., which was discussed to originate either from an unexpectedly intense hot band or



**Fig. 1** Mass spectrum of the pyrolyzed quadricyclane precursor at hv = 9.5 eV and a pyrolysis temperature of 740 K. Pyrolysis selectively yields cyclopropenylidene (m/z=38) and benzene (m/z=78). The peak at m/z=109 corresponds to 3-methoxypyridine employed in a previous experiment.



DOI: 10.1039/C6CP01068G

ARTICLE

**Fig. 2** Mass-selected threshold photoelectron spectrum of cyclopropenylidene. The Franck-Condon simulation (blue sticks; red line: convolution with Gaussian fwhm=30 meV) assuming a vibrational temperature of 740 K confirms that the cooling of the generated pyrolysis products in the continuous molecular beam is negligible.

more likely, the contribution of another isomer, propargylene HCCCH.<sup>5</sup> The new TPE spectrum confirms the latter explanation, as the band at 9.02 eV is almost completely suppressed with the quadricyclane precursor (Fig. 2). The data enable us to determine the absolute photoionization cross section of cyclopropenylidene by the following relation:

$$\frac{S_{C_3H_2}}{S_{C_6H_6}} = \frac{[C_3H_2]}{[C_6H_6]} \cdot \frac{\sigma_i^{C_3H_2}}{\sigma_i^{C_6H_6}} \cdot \frac{A_{C_3H_2}}{A_{C_6H_6}}$$
(1)

S stands for the detected ion signals of the respective species,  $[C_3H_2]$  and  $[C_6H_6]$  correspond to the concentrations of cyclopropenylidene and benzene,  $\sigma_i$  is the absolute photoionization cross section, and A represents the apparatus functions. As the two pyrolysis products are generated in a 1:1 ratio, the fraction of the species concentrations equals 1. The apparatus function comprises a mass-dependent element, the so-called mass discrimination factor.<sup>56</sup> As shown in the Electronic Supplementary Information (ESI), the mass discrimination factor can be approximated to be comparable for m/z = 38 and m/z = 78 and the ratio of apparatus function terms in equation (1) is close to unity. Since the employed continuous molecular beam has an effusive character, the sampling efficiency is mass independent and the mass dependence of the channel plate gain is small over the investigated mass range. The Franck-Condon simulation of the carbene's TPE spectrum at T=740 K, the pyrolysis temperature, agrees well with the experimental spectrum, as illustrated in Fig. 2 and supports the assumption of an effusive beam.<sup>57, 58</sup> Thus, equation (1) reduces to:

$$\sigma_i^{C_3H_2} = \frac{S_{C_3H_2}}{S_{C_6H_6}} \cdot \sigma_i^{C_6H_6} \tag{2}$$

The absolute photoionization cross section of c-C<sub>3</sub>H<sub>2</sub> was then determined normalizing the PIE curve of benzene on the absolute photoionization cross section reported in the literature by Cool et al.<sup>10</sup> These literature values of Cool et al.

#### ARTICLE

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42.

were obtained by measuring the benzene cross section in a binary mixture relative to propene and were afterwards normalized to the previously determined curve of Rennie et al.,<sup>21</sup> who used nitrogen oxide as a reference. To evaluate the influence of the beam temperature on the cross sections, we recorded PIE curves of benzene at various temperatures (see Fig. S2). The obtained photoionization cross section for cyclopropenylidene as a function of the photon energy is depicted in Fig. 3 (see ESI for the tabulated values). Steps in the respective PIE curves are observed at the ionization energies for cyclopropenylidene and benzene. The non-zero ion signal below the IE indicate that pyrolysis products are generated vibrationally hot, which is expected for this experimental setup. Note that, as discussed in the experimental section, it is only possible to determine the cross section for ions generated with an excess energy less than about 1 eV due to the limited size of the electron imaging detector.

We now analyse the various sources of errors for the absolute photoionization cross section of cyclopropenylidene given in Fig. 3. The first source is the assumption of an effusive beam and mass-independent apparatus function. As discussed further in the ESI, the associated error seems to be small. Further error sources are the integration limits for the studied mass peaks (including the <sup>13</sup>C isotopologues), the subtraction of false coincidences, and the normalization of benzene's recorded photoion yield curve above the IE to the absolute photoionization cross section of Cool et al.<sup>10</sup> The value of benzene's cross section itself accounts by far for the greatest source of error, because its uncertainty is stated to be 20 %.<sup>10</sup> The overall error for the absolute photoionization cross section reported in this paper is therefore evaluated to be around ±30 % of  $\sigma_i$ , indicated in grey in Fig. 3. In comparison to other open-shell hydrocarbons like methyl<sup>16</sup> or ethyl,<sup>18</sup> the cross section of cyclopropenylidene shows a faster increase above the ionization threshold.

Page 4 of 8

#### 3.2 Dissociative Photoionization

A previous investigation of the DPI of c-C<sub>3</sub>H<sub>2</sub> using 1chlorocycloprop-2-ene as the precursor was challenged by the presence of HCl, which appears as a direct product after  $\alpha$ elimination.<sup>5, 44, 45</sup> The  $H^{37}$ Cl isotopologue has the same m/zratio as cyclopropenylidene and therefore contributes to the parent ms-TPE signal. A disentanglement of the two contributions to the m/z = 38 channel therefore requires a subtraction of the HCl signal weighted by an empirical factor that includes the Cl isotopic ratio, which introduces a significant source of error. Employing the quadricyclane precursor, it is hence possible to investigate the dissociative photoionization of cyclopropenylidene by analysing the massselected TPE spectra without this perturbation. Cyclopropenylidene undergoes dissociative photoionization at higher photon energies to form a daughter ion of m/z = 37, i.e. a hydrogen atom loss to  $C_3H^{\scriptscriptstyle +}$  takes place. A breakdown diagram for the dissociative photoionization of c-C<sub>3</sub>H<sub>2</sub> was recorded between 12.5 and 14.2 eV. In Fig. 4, the fractional abundances of the parent and daughter ion's TPE signal are plotted as a function of the photon energy. The simultaneously recorded TOF distribution shows no asymmetry for the daughter ion peak (see ESI), which indicates that the dissociation is fast and there is no kinetic shift. The 0 K appearance energy is the photon energy at which even the initially 0 K neutrals gain enough internal energy to dissociatively photoionize. The parent ion's disappearance energy corresponds to the 0 K appearance energy of the lowest lying dissociative photoionization channel in small molecules and in the absence of a kinetic shift.<sup>59, 60</sup>

The signal/noise ratio is very low due to unfavourable Franck-Condon factors in the investigated energy range presumably because no excited cationic state of  $c-C_3H_2^+$  is close in energy. A decrease of the parent signal (m/z = 38) is observed with a simultaneous rise of the daughter ion signal (m/z = 37), setting in around 12.9 eV. The parent ion signal drops to zero at



Fig. 3 Absolute photoionization cross section of cyclopropenylidene (black curve), which was generated in stoichiometric quantities from the quadricyclane precursor. The second fragment is benzene (red curve), which acts as reference cross section. The margin of error for the cross section is indicated by the shaded grey area and evaluated to be ±30%.



**Fig. 4** Breakdown diagram of the dissociative photoionization of cyclopropenylidene to  $HCCC^*$  (black squares: parent ion m/z = 38; red circles: daughter ion m/z = 37). Two fits of the breakdown curves are shown for temperatures of T=740 K (dotted lines, daughter blue) and T=1200 K (solid lines, daughter red) (see discussion for details).

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42

#### Journal Name

around 13.6 eV. Due to the absence of a kinetic shift the parent ion's energy of disappearance should therefore correspond the appearance energy  $AE_{0K}(C_3H_2; C_3H^{+})$ .<sup>59</sup>

Quantum chemistry was employed to analyse further the dissociative photoionization of cyclopropenylidene to  $C_3H^{\dagger}$ . In agreement with previous theoretical studies,<sup>36</sup> the direct product of H atom loss, cyclic  $C_3H^+$  was found to be a transition state on the way to the linear isomers HCCC<sup>+</sup> on the B3LYP/6-311G(d,p) level of theory. The activation barrier for the dissociation via the cyclic  $C_3H^+$  cationic transition state is predicted to lie at +14.29 eV relative to neutral  $c-C_3H_2$  and 5.12 eV above  $c-C_3H_2^+$  (CBS-QB3). This value is significantly higher than the observed energy of disappearance for the parent ion at around 13.6 eV. A rearrangement of the dissociating ion to another isomer must therefore be considered.  $\mathsf{HCCCH}^{^+}$  and  $\mathsf{H_2CCC}^{^+}$  were found to represent further stable isomers of the composition  $C_3H_2^+$  (see Fig. 5), in agreement with the literature.<sup>36</sup> The former one is computed to be only 0.25 eV (24 kJ mol<sup>-1</sup>) less stable than c-C<sub>3</sub>H<sub>2</sub><sup>+</sup>. Wong and Radom reported an activation barrier of 1.75 eV for the isomerization of c-C<sub>3</sub>H<sub>2</sub> to HCCCH<sup>+</sup> as computed on the MP2/6-31G(d) level. This transition state could not be localized in the present study, but CASSCF calculations yielded a potential energy curve suggesting a conical intersection in this energy range. Subsequent hydrogen atom loss was found to proceed without a reverse barrier, but necessitating a significantly higher activation energy of 4.18 eV relative to the HCCCH<sup>+</sup> structure. An isomerization barrier of 3.29 eV is predicted for the rearrangement of  $c-C_3H_2^+$  to  $H_2CCC^+$ , which lies 1.96 eV (189 kJ mol<sup>-1</sup>) higher in energy than the cyclic cation. The H atom loss again proceeds without a reverse barrier leading to the same products as the pathway involving the HCCCH<sup>+</sup> isomer. Yielding the same fragments without an overall reverse barrier (see Fig. 5), both pathways are calculated to have the same appearance energy of 13.60 eV at the CBS-QB3 level of theory. This value could be confirmed by other composite methods, namely CBS-APNO (13.64 eV), W1U (13.70 eV), and G3 (13.58 eV), employing different geometry optimization and electron correlation approaches. As discussed above, the TOF distributions indicate a fast dissociation on the timescale of the experiment. The parent  $(BD_P)$  and daughter  $(BD_D)$  ion signal in the breakdown diagram can then be modelled using the following expressions:<sup>55</sup>

$$BD_{P}(hv) = \int_{0}^{AE-hv} P(E)dE$$

$$BD_{D}(hv) = \int_{AE-hv}^{\infty} P(E)dE \text{ for } hv < AE$$
(3)

$$D_P(h\nu) = 0$$
(4)  

$$BD_D(h\nu) = 1 \text{ for } h\nu > AE$$



View Article Online DOI: 10.1039/C6CP01068G

Fig. 5 Computed mechanism for the dissociative photoionization of cyclopropenylidene to HCCC<sup>+</sup>.

Here, P(E) is the thermal energy distribution of the dissociating ion, which is assumed to be a Boltzmann distribution that can be calculated based on the density of states (DOS) of neutral cyclopropenylidene.<sup>55</sup> In RRKM (Rice-Ramsperger-Kassel-Markus) calculations, the isomerization rates for both pathways to H<sub>2</sub>CCC<sup>+</sup> and HCCCH<sup>+</sup> were found to be several orders of magnitude higher at the energy of the dissociation threshold than the rates for the respective hydrogen loss step. Consequently, the rearrangement of the cation does not influence the modelling of the breakdown diagram. Using phase space theory, the dissociation rate at threshold energy was computed to be  $5 \cdot 10^9 \text{ s}^{-1}$  for H<sub>2</sub>CCC<sup>+</sup> and  $5 \cdot 10^6 \text{ s}^{-1}$  for HCCCH<sup>+</sup>, respectively. Therefore, the dissociation is fast on the timescale of the experiment, regardless whether  $H_2CCC^+$  or  $HCCCH^+$  is the dissociating ion, with calculations suggesting that the former pathway is favoured. The proposed dissociation mechanism is in good agreement with the experimentally observed fast dissociation rate, as visible from the symmetric TOF distribution.

The breakdown diagram was then fitted using equation (3) and (4) by setting the neutral temperature to T=740 K, as obtained from the Franck-Condon simulation of the TPE spectrum (Fig. 2), calculating the internal energy distribution of the neutral, and shifting it by the photon energy to obtain the fractional abundances of the parent and daughter ions, i.e. the fraction of the distribution below and above the dissociation threshold, at each photon energy. Assuming a vibrational temperature of 740 K yielded the best fit to the high-energy part of the breakdown diagram and an  $AE_{0K}$  of 13.67 eV, as depicted as a dashed line in Fig. 4. However, the measured daughter ion abundances between 13.0 and 13.5 eV are significantly underestimated by the model. In fact, the best agreement between experiment and fit at the low energy side was obtained for a temperature of T = 1200 K, which is shown as a full line in Fig. 4. We want to emphasize that such a high temperature is not only in contrast with the absence of hot bands in the TPE spectrum (see ESI), it is also unrealistically high for a 740 K pyrolysis experiment, as confirmed by the TPE spectrum modelling. Anharmonicity leads to a higher density of states at high internal energies, and may increase the abundance of high-energy neutrals considerably already at temperatures of 700-800 K. We therefore expect anharmonicity to be the main reason of the temperature discrepancy. Second, in modelling the breakdown diagram, we assume that the internal energy distribution of the neutral is shifted by the photon energy onto the ionic manifold without being distorted. In other words, we assume that the threshold photoionization cross section is independent of the internal



#### ARTICLE

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42.

energy. While this has proven to be a generally reliable assumption in room temperature or colder systems,<sup>55</sup> small deviations have been observed.<sup>61</sup> If the threshold photoionization cross-section for hot neutrals at high photon energies were up to an order of magnitude larger than for rovibrationally cold ones, the increased width of the breakdown diagram could be explained. While this reason cannot be ruled out, the fact that up to a factor ten enhancement would be needed for the hot neutrals, we think it is unlikely that it plays an important role in the broadening of the breakdown diagram. Third, depending on the reaction coordinate, the pyrolysis products may be formed with significant vibrational excitation energy in certain modes. If rethermalization in the pyrolysis source were inefficient and vibrational cooling in the molecular beam expansion negligible, this vibrational excess energy could remain trapped in the pyrolysis products. However, it has been observed several times that re-thermalization by collisional heating is prompt under our pyrolysis conditions,<sup>62, 63</sup> which makes it highly unlikely that collisional cooling is slow and that this effect plays any role in the temperature discrepancy. Furthermore, the breakdown diagram obtained after manual subtraction of the HCl signal in experiments using the 1-chlorocycloprop-2-ene precursor also required an unrealistically high temperature for the fit,<sup>26</sup> and it is also unlikely that the two different reaction coordinates should lead to the deposition of similar amounts of excess internal energy in the product carbene. A last, rather remote possibility is that the dissociative photoionization of the unconverted precursor affects m/z = 37 smoothly, which in the end yields a breakdown diagram of apparently higher temperature. The chances for this affecting several hightemperature breakdown diagrams are minuscule and computations on the precursor's DPI do not support this hypothesis. None of these explanations challenge the validity of the computationally confirmed experimental appearance energy of  $C_3H^{\dagger}$  from cyclopropenylidene. We therefore accept the low-temperature fit value of  $AE_{0\kappa}(c-C_3H_2;$  $C_3H^+$ )=13.67±0.10 eV because it describes best the region where the parent ion signal drops to zero and is in agreement with our own calculations as well as a recent theoretical paper.

Utilizing this appearance energy, the heat of formation of cyclopropenylidene  $\Delta_{f}H_{OK}(c-C_{3}H_{2}) = 501 \pm 9 \text{ kJ mol}^{-1}$  (converted from the 298 K value of Chyall and Squires<sup>64</sup> using the W1U thermal enthalpy and in very good agreement with high-level computations by Lau and Ng<sup>65</sup>) and the ionization energy for linear C<sub>3</sub>H determined by Kaiser et al. as IE(*I*-C<sub>3</sub>H) = 9.15±0.05 eV,<sup>66</sup> the heat of formation of *I*-C<sub>3</sub>H can be determined in a thermochemical cycle:

$$\Delta_f H_{0K}(C_3 H) = \Delta_f H_{0K}(C_3 H_2) + AE(C_3 H^+)$$
(5)  
$$-\Delta_f H_{0K}(H) - IE(C_3 H)$$

The obtained value of 725 ± 24 kJ mol<sup>-1</sup> lies above the first estimation of Saturno from the C-H bonding dissociation energy of  $C_3H_3$  and  $C_3H_2$  (583 kJ mol<sup>-1</sup>).<sup>67</sup> However, the heats of formation of c- $C_3H_2$  and propargyl<sup>68</sup> ( $\Delta_f H_{OK}(C_3H_3) = 342 \pm 4$  kJ mol<sup>-1</sup> converted from room temperature using the W1U

thermal enthalpy), together with the W1U (and W1Usc) calculated 0 K ½ H<sub>2</sub> and H<sub>2</sub> abstraction energies of 230 (224) and 369 (367) kJ mol<sup>-1</sup>, yield, on average,  $\Delta_f H_{0k}(C_3H) = 719 \pm 11 \text{ kJ mol}^{-1}$ , in good agreement with the newly determined experimental value. For the C<sub>3</sub>H<sup>+</sup> cation, an experimental heat of formation of  $\Delta_f H_{0k}(C_3H^+) = 1604 \pm 19 \text{ kJ mol}^{-1}$  is obtained.

#### 4. Conclusions

The absolute photoionization cross section of cyclopropenylidene was determined and its dissociative photoionization was investigated using imaging photoelectron photoion coincidence spectroscopy. A quadricyclane precursor was employed, which yields benzene and the desired carbene in stoichiometric quantities. Absolute photoionization cross sections of cyclopropenylidene up to 9.8 eV were derived from the photoionization yield curves and the known cross section of benzene. The absolute cyclopropenylidene photoionization cross section at 9.5 eV, for example, was found to be 4.5  $\pm$ 1.4 Mb.

Dissociative photoionization of cyclopropenylidene to  $C_3H^+$  was observed in the mass-selected threshold photoelectron spectra. Computations reveal that the cyclopropenylidene cation first isomerizes to HCCCH<sup>+</sup> or H<sub>2</sub>CCC<sup>+</sup>, before an H atom loss occurs, leading in both cases to linear C<sub>3</sub>H<sup>+</sup>. Based on the symmetric and narrow daughter ion TOF peak shapes, the dissociation is fast on the experimental time scale. The breakdown diagram is markedly broader than expected based on the cyclopropenylidene internal energy distribution calculated within the harmonic approximation at the estimated sample temperature of 740 K. Significant anharmonicity is suggested to be the main reason for the broadening of the internal energy distribution, and increasing threshold photoionization cross sections with increasing internal energy of the neutral as well as a non-Boltzmann internal energy distribution due to vibrational excitation along the pyrolysis reaction coordinate are also discussed. The breakdown diagram fit, using a realistic temperature, yields an appearance energy of  $AE_{0K}(c-C_3H_2; C_3H^+)=13.67\pm0.10 \text{ eV}$ , as confirmed by several computations with independent methods. The appearance energy of  $C_3H^+$  enables to derive the heat of formation for neutral and ionic I-C3H via a thermochemical cycle and we obtained values of  $\Delta_{f}H_{OK}(C_{3}H) =$ 725 ± 25 kJ mol<sup>-1</sup> and  $\Delta_f H_{0K}(C_3 H^{+}) = 1604 \pm 19$  kJ mol<sup>-1</sup>.

#### Acknowledgement

The experiments were conducted at the VUV beamline of the Swiss Light Source storage ring, Paul Scherrer Institute. We acknowledge the assistance of Isabella Wagner and Engelbert Reusch during the experiments. The work was supported by the Deutsche Forschungsgemeinschaft, contract FI575/7-3, the GRK 1221, and the Swiss Federal Office for Energy (BFE Contract Number 101969/152433 & SI/501269-01). Travel subsidies were provided by the European Commission

DOI: 10.1039/C6CP01068G

Phys. Chem. Chem. Phys.

Published on 09 March 2016. Downloaded on 10/03/2016 07:08:42

#### **Physical Chemistry Chemical Physics**

#### Journal Name

program "CALIPSO Transnational Access". Computations were performed at the Linux-cluster of the Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften (LRZ) and the Merlin 4 HPC cluster at PSI.

#### References

- C. A. Taatjes, S. J. Klippenstein, N. Hansen, J. A. Miller, T. A. Cool, J. Wang, M. E. Law and P. R. Westmoreland, *Phys. Chem. Chem. Phys.*, 2005, **7**, 806–813.
- H. Clauberg, D. W. Minsek and P. Chen, J. Am. Chem. Soc., 1992, 114, 99–107.
- 3. H. Clauberg and P. Chen, J. Phys. Chem., 1992, **96**, 5676– 5678.
- 4. H. Clauberg and P. Chen, J. Am. Chem. Soc., 1991, **113**, 1445-1446.
- P. Hemberger, B. Noller, M. Steinbauer, I. Fischer, C. Alcaraz, B. K. Cunha de Miranda, G. A. Garcia and H. Soldi-Lose, J. Phys. Chem. A, 2010, **114**, 11269–11276.
- 6. S. J. Klippenstein, J. A. Miller and A. W. Jasper, *J. Phys. Chem. A*, 2015, **119**, 7780-7791.
- T. A. Cool, J. Wang, N. Hansen, P. R. Westmoreland, F. L. Dryer, Z. Zhao, A. Kazakov, T. Kasper and K. Kohse-Höinghaus, *Proc. Combust. Inst.*, 2007, **31**, 285-293.
- C. A. Taatjes, N. Hansen, D. L. Osborn, K. Kohse-Höinghaus, T. A. Cool and P. R. Westmoreland, *Phys. Chem. Chem. Phys.*, 2008, **10**, 20–34.
- 9. J. Berkowitz, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy*, Academic Press, New York, 1979.
- 10. T. A. Cool, J. Wang, K. Nakajima, C. A. Taatjes and A. McIlroy, *Int. J. Mass Spectrom.*, 2005, **247**, 18–27.
- 11. J. C. Robinson, N. E. Sveum and D. M. Neumark, *J. Chem. Phys.*, 2003, **119**, 5311–5314.
- 12. J. D. Savee, S. Soorkia, O. Welz, T. M. Selby, C. A. Taatjes and D. L. Osborn, *J. Chem. Phys.*, 2012, **136**, 134307.
- H. Xu and S. T. Pratt, J. Phys. Chem. A, 2013, 117, 9331– 9342.
- 14. J. C. Robinson, N. E. Sveum and D. M. Neumark, *Chem. Phys. Lett.*, 2004, **383**, 601–605.
- 15. N. E. Sveum, S. J. Goncher and D. M. Neumark, *Phys. Chem. Chem. Phys.*, 2006, **8**, 592–598.
- B. Gans, L. A. V. Mendes, S. Boyé-Péronne, S. Douin, G. Garcia, H. Soldi-Lose, B. K. Cunha de Miranda, C. Alcaraz, N. Carrasco, P. Pernot and D. Gauyacq, J. Phys. Chem. A, 2010, 114, 3237–3246.
- 17. J.-C. Loison, J. Phys. Chem. A, 2010, **114**, 6515-6520.
- B. Gans, G. A. Garcia, S. Boyé-Péronne, J.-C. Loison, S. Douin, F. Gaie-Levrel and D. Gauyacq, *J. Phys. Chem. A*, 2011, **115**, 5387–5396.
- H. P. Reisenauer, G. Maier, A. Riemann and R. W. Hoffmann, *Angew. Chem. Int. Ed.*, 1984, 23, 641.
- M. S. Schuurman, J. Giegerich, K. Pachner, D. Lang, B. Kiendl, R. J. MacDonell, A. Krueger and I. Fischer, *Chem. Eur. J.*, 2015, **21**, 14486–14495.
- E. E. Rennie, C. A. F. Johnson, J. E. Parker, D. M. P. Holland, D. A. Shaw and M. A. Hayes, *Chem. Phys.*, 1998, 229, 107–123.
- 22. L. A. Chewter, M. Sander, K. Müller-Dethlefs and E. W. Schlag, *J. Chem. Phys.*, 1987, **86**, 4737–4744.

- 23. T. Schüßler, H.-J. Deyerl, S. Dümmler, I. Fischer, C. Alcaraz and M. Elhanine, *J. Chem. Phys.*, 2003, **118**, 9077–9080.
- 24. I. Fischer, T. Schüßler, H.-J. Deyerl, M. Elhanine and C. Alcaraz, *Int. J. Mass Spectrom.*, 2007, **261**, 227–233.
- 25. T. Schüßler, W. Roth, T. Gerber, I. Fischer and C. Alcaraz, *Phys. Chem. Chem. Phys.*, 2005, **7**, 819–825.
- 26. P. Hemberger, Dissertation, Julius-Maximilians Universität Würzburg, 2011.
- 27. T. G. Rowland, S. Borkar, A. Bodi and B. Sztáray, *Int. J. Mass Spectrom.*, 2015, **378**, 134-142.
- J. Bouwman, B. Sztáray, J. Oomens, P. Hemberger and A. Bodi, J. Phys. Chem. A, 2015, 119, 1127–1136.
- J. M. Vrtilek, C. A. Gottlieb and P. Thaddeus, *ApJ*, 1987, 314, 716–725.
- P. Thaddeus, J. M. Vrtilek and C. A. Gottlieb, *ApJ*, 1985, 299, L63-L66.
- P. Cox, R. Guesten and C. Henkel, Astron. Astrophys., 1987, 181, L19-L22.
- P. Cox, R. Guesten and C. Henkel, Astron. Astrophys., 1988, 206, 108-116.
- 33. P. Cox, C. M. Walmsley and R. Guesten, *Astron. Astrophys.*, 1989, **209**, 382-390.
- 34. S. C. Madden, W. M. Irvine, D. A. Swade, H. E. Matthews and P. Friberg, *AJ*, 1989, **97**, 1403-1422.
- 35. N. G. Adams and D. Smith, *ApJ*, 1987, **317**, L25-L27.
- M. W. Wong and L. Radom, J. Am. Chem. Soc., 1993, 115, 1507–1514.
- D. Gerlich and S. Horning, *Chem. Rev.*, 1992, **92**, 1509– 1539.
- S. D. Prodnuk, S. Grocert, V. M. Bierbaum and C. H. DePuy, Org. Mass Spectrom., 1992, 27, 416–422.
- G. B. I. Scott, D. A. Fairley, C. G. Freeman, M. J. McEwan, N. G. Adams and L. M. Babcock, *J. Phys. Chem. A*, 1997, 101, 4973–4978.
- 40. J. P. Sánchez, N. F. Aguirre, S. Díaz-Tendero, F. Martín and M. Alcamí, *J. Phys. Chem. A*, 2016, **120**, 588–605.
- J. Pety, P. Gratier, V. Guzmán, E. Roueff, M. Gerin, J. R. Goicoechea, S. Bardeau, A. Sievers, F. Le Petit, J. Le Bourlot, A. Belloche and D. Talbi, *Astron. Astrophys.*, 2012, **548**, A68.
- A. M. Brett, P. B. Carroll, A. L. Ryan, A. B. Geoffrey, M. H. Jan, J. L. Frank, R. J. Philip and J. R. Anthony, *ApJ*, 2013, **774**, 56.
- P. Botschwina, C. Stein, P. Sebald, B. Schröder and R. Oswald, ApJ, 2014, **787**, 72.
- 44. P. Hemberger, B. Noller, M. Steinbauer, K. Fischer and I. Fischer, J. Phys. Chem. Lett., 2010, 1, 228–231.
- P. Hemberger, J. Kohler, I. Fischer, G. Piani, L. Poisson and J.-M. Mestdagh, *Phys. Chem. Chem. Phys.*, 2012, 14, 6173–6178.
- 46. M. Johnson, A. Bodi, L. Schulz and T. Gerber, *Nucl. Instr. Meth. Phys. Res. A*, 2009, **610**, 597–603.
- 47. A. Bodi, M. Johnson, T. Gerber, Z. Gengeliczki, B. Sztáray and T. Baer, *Rev. Sci. Instrum.*, 2009, **80**, 034101.
- 48. A. Bodi, P. Hemberger, T. Gerber and B. Sztáray, *Rev. Sci.* Instrum., 2012, **83**, 083105.
- D. W. Kohn, H. Clauberg and P. Chen, *Rev. Sci. Instrum.*, 1992, 63, 4003–4005.
- 50. B. Sztáray and T. Baer, *Rev. Sci. Instrum.*, 2003, **74**, 3763– 3768.
- J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski and G.
   A. Petersson, J. Chem. Phys., 1999, 110, 2822–2827.

#### ARTICLE

- J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski and G. A. Petersson, J. Chem. Phys., 2000, **112**, 6532–6542.
- 53. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 54. V. A. Mozhayskiy and A. I. Krylov, ezSpectrum, http://iopenshell.usc.edu/downloads.
- B. Sztáray, A. Bodi and T. Baer, J. Mass Spectrom., 2010, 45, 1233–1245.
- 56. J. D. Bittner, Dissertation, Massachusetts Institute of Technology, 1981.
- B. K. Cunha de Miranda, C. Alcaraz, M. Elhanine, B. Noller, P. Hemberger, I. Fischer, G. A. Garcia, H. Soldi-Lose, B. Gans, L. A. V. Mendes, S. Boyé-Péronne, S. Douin, J. Zabka and P. Botschwina, *J. Phys. Chem. A*, 2010, **114**, 4818– 4830.
- J. D. Savee, J. Zádor, P. Hemberger, B. Sztáray, A. Bodi and D. L. Osborn, *Mol. Phys.*, 2015, **113**, 2217-2227.
- 59. T. Baer, Int. J. Mass Spectrom., 2000, 200, 443–457.
- T. Baer, A. Guerrero, J. Z. Davalos and A. Bodi, *Phys. Chem. Chem. Phys.*, 2011, 13, 17791-17801.
- 61. A. Bodi, N. S. Shuman and T. Baer, *Phys. Chem. Chem. Phys.*, 2009, **11**, 11013–11021.
- S. Liang, P. Hemberger, N. M. Neisius, A. Bodi, H. Grützmacher, J. Levalois-Grützmacher and S. Gaan, *Chem. Eur. J.*, 2015, **21**, 1073–1080.
- F. Holzmeier, I. Wagner, I. Fischer, A. Bodi and P. Hemberger, J. Phys. Chem. A, 2015, DOI: 10.1021/acs.jpca.5b10743.
- 64. L. J. Chyall and R. R. Squires, *Int. J. Mass Spectrom. Ion Proc.*, 1995, **149/150**, 257.
- 65. K. C. Lau and C. Y. Ng, *Chin. J. Chem. Phys.*, 2006, **19**, 29-38.
- R. I. Kaiser, L. Belau, S. R. Leone, M. Ahmed, Y. Wang, B. J. Braams and J. M. Bowman, *ChemPhysChem*, 2007, 8, 1236-1239.
- 67. A. F. Saturno, *NASA Tech. Memo.*, 1982, **84537**.
- W. Tsang, in *Energetics of Organic Free Radicals*, eds. J. A. Martinho Simoes, A. Greenberg and F. F. Liebman, Blackie Academic and Professional, London, 1996, pp. 22-58.

Page 8 of 8