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3 Ion Dissociation Dynamics of 1,2,3,4-Tetrahydronaphthalene: Tetralin as
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7 a Test Case For Hydrogenated PAHs
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ABSTRACT: The unimolecular dissociation of ionized tetralin was probed by tandem mass spectrometry, imaging photoelectron photoion coincidence (iPEPICO) spectroscopy and theory. The major reactions observed were the loss of the hydrocarbons $\text{CH}_3^\bullet$, C_2H_4 and $\text{C}_3\text{H}_5^\bullet$ together with $\text{H}^\bullet$ atom loss. RRKM modeling of the iPEPICO data suggested a two well potential energy surface. Ionized tetralin can lose all four neutrals via H-shift and ring-opening reactions, or $\text{CH}_3^\bullet$ and C_2H_4 after interconversion to the 1-methylindane ion, a process similar to that found for ionized 1,2-dihydronaphthalene (isomerizing to form the 1-methylindene ion structure). This was confirmed at the B3LYP/6-31+G(d,p) level of theory and potential mechanisms for all reactions are described. The ionization energy of tetralin was established from the threshold photoelectron spectrum to be 8.46 ± 0.01 eV.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic molecules suggested to constitute roughly 20% of carbon in the interstellar medium (ISM).¹ These species exist in both neutral and ionic forms and both are potentially involved in processes such as H₂ formation and the shielding of organic chemical reactions from high energy radiation.² PAHs in the ISM can absorb UV light from stars, initiating photodissociation to form important interstellar molecules. Molecular H₂ is the most prolific molecular species found in the interstellar medium (ISM). Whereas it has been long recognized that H₂ is formed on dust grains,³ investigation of the involved mechanisms is still a very active subject of research.^{4,5} One popular theory is that polycyclic aromatic hydrocarbons (PAH) may play a role in the formation of H₂ by acting as catalysts.¹ Atomic hydrogen would adsorb onto the surface of the molecules, thus hydrogenating the PAHs, prior to desorption of H₂.⁶⁻¹¹ This reaction demonstrates the importance of investigating the energetics of not only PAHs but modified PAHs as well, such as hydrogenated species.

There has been very little work done on superhydrogenated PAHs. A theoretical study was conducted on protonated naphthalene which had the H⁺ loss at an activation energy of 2.71 eV which is in good agreement with that for H⁺ loss from dihydronaphthalene.¹² Reitsma et al. have also shown the effect of hydrogenation on coronene using soft x-ray spectroscopy; they showed that hydrogenation under these high energy conditions acts as a protector for the carbon backbone.¹³ The opposite was observed for ionized hydrogenated pyrene studied at high energy collision-induced dissociation (CID) mass spectrometry and action spectroscopy. Here, it was observed that the appearance energy for CH₃⁺-loss decreased with increasing hydrogenation.¹⁴⁻

¹⁶ Hydrogenation of coronene has been explored.¹⁷⁻¹⁹ We previously studied 1,2-

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3 dihydronaphthalene and 9,10-dihydrophenanthrene by the imaging photoelectron photoion
4 coincidence (iPEPICO) technique.²⁰ Unlike PAH ions, which display unimolecular losses of H[•]
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6 (both directly and sequentially) and acetylene, the two dihydroPAH ions undergo reactions
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8 leading to loss of H[•] and CH₃[•]. Both were found to isomerize to a methyindene analogue at low
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10 internal energies, allowing for H[•] and CH₃[•]-loss, but as internal energy increases this channel was
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12 outcompeted by direct H[•]-loss from the molecular ion. No H₂ was formed in the decomposition
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14 of these ions.
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20 In light of the results for dihydroPAH ions, we have examined the unimolecular reactions
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22 of ionized 1,2,3,4-tetrahydronaphthalene, or tetralin, by iPEPICO spectroscopy and tandem mass
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24 spectrometry to explore the possibility of H₂ formation from polyhydrogenated precursors.
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26 Tetralin, with chemical formula C₁₀H₁₂, is one of the smallest superhydrogenated PAHs and is a
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28 component of jet²¹ and diesel²² fuels. The unimolecular decomposition of neutral tetralin was
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30 previously studied at high temperature under single-pulse shock-tube conditions (1000–1400K)
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32 by Tsang and Cui,²³ who determined rates for channels resulting in the formation of ethylene +
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34 benzocyclobutene and *o*-allyltoluene. Tetralin is also an intermediate in the synthesis of
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36 agricultural chemicals and a good hydrogen donor in the fuel cells.²⁴⁻²⁶ So, the question arises if
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38 it can be a hydrogen donor in the ISM.
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47 EXPERIMENTAL METHODS

48 TANDEM MASS SPECTROMETRY

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50 Atmospheric pressure chemical ionization (APCI) experiments were performed on a Micromass
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52 Quattro Ultima (Waters Micromass, Manchester, U.K.) triple quadrupole mass spectrometer
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equipped with a Z-spray source. Tetralin was purchased from Sigma-Aldrich (Sigma-Aldrich, Oakville, ON, CA, >97% purity) and used without further purification. Compounds were dissolved in chlorobenzene to produce a $100 \mu\text{g mL}^{-1}$ solution.²⁷ This solution was delivered to the APCI source by syringe pump at a flow rate of $50 \mu\text{L min}^{-1}$. The source block and probe temperatures were 80°C and 400°C , respectively, while the corona and cone voltages were 4.0 kV and 40 V. The quadrupole resolution was set to 18 in the Masslynx software to provide baseline separation of all peaks, resulting in a mass resolution ($m/\Delta m$) of 100. Collision-induced dissociation (CID) was carried out using argon collision gas at a pressure of approximately 7.8×10^{-4} mbar over a laboratory-frame collision energy (E_{lab}) range of 0 to 31 eV.

IMAGING PHOTOELECTRON PHOTOION COINCIDENCE SPECTROSCOPY (IPEPICO)

iPEPICO spectroscopy experiments were conducted on the VUV beamline at the Swiss Light Source (SLS, Paul Scherrer Institut, Villigen, Switzerland) and have been described in detail elsewhere and only a brief description will be provided here.²⁸⁻³⁰

Tetralin was thermally volatilized at 25°C into the photon interaction region with a heated oven and photoionized by monochromatic synchrotron radiation (4–8 meV resolution depending on the photon energy).³¹ Photoions and photoelectrons are extracted using a weak electric field of 218 V/cm. The photoions are accelerated toward a time-of-flight (TOF) mass spectrometer, while the ejected electrons are velocity-mapped on an imaging RoentDek delay line detector. The electrons are time- and position-stamped at the detector and the corresponding photoions are detected in delayed coincidence. Threshold electrons account for the majority of the signal at the center of the multichannel plate, MCP, detector whereas non-zero-kinetic energy electrons are

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3 mostly detected according to their off-axis momentum. Some of the non-zero-kinetic energy
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5 electrons will have the proper trajectory to hit the center spot, therefore the mass spectrum
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7 based on electrons detected in a ring around the center spot is used to account for this 'hot
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9 electron' contamination. The ions detected in coincidence with electrons arriving in the ring can
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11 then be subtracted from ions detected in coincidence with the electrons that appeared in the
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13 center to obtain the threshold photoionization mass spectrum.³² Photoions are space-focussed
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15 onto the detector, resulting in a mass resolution of $\Delta m/m=270$. The photon energy range used
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17 for the photoelectron spectrum was 8.3 – 15.5 eV, with data points taken every 0.05 eV. Longer
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19 accumulation times were used for points between 10 and 13.5 eV for the breakdown diagram
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21 measurement.
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28 The TOF mass spectrometer consists of two acceleration regions, one with a low draw out
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30 potential that allows ions dissociating on the microsecond time scale to do so while being
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32 accelerated. This results in asymmetric time-of-flight peaks for product ions that form from the
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34 parent ion that dissociates as it propagates down the flight tube, which can be modeled to extract
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36 unimolecular decay rate constants as a function of photon energy. When multiple product ions
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38 are generated, they are all formed with the same overall effective decomposition rate constant
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40 of the precursor ion, and the fractional fragment ion abundances, i.e., the branching ratios, can
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42 be used to apportion absolute dissociation rates to each of the decay channels. This way,
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44 dissociation rate constants are obtained for all channels on the basis of the asymmetric peak
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46 profile of just one fragment ion.
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COMPUTATIONAL METHODS

Geometry optimizations and harmonic vibrational frequency calculations of all species and transition states were conducted using the Gaussian 16 package³³ at the B3LYP/6-31+G(d,p) level of theory. Transition states were confirmed with the intrinsic reaction coordinate (IRC) protocol. Franck–Condon simulations utilized the double harmonic approximation.³⁴ Molecular orbital energies were calculated using the Outer Valence Green's Function Method at the OVGF/cc-pVTZ level of theory.

The minimalPEPICO program was used to fit the iPEPICO breakdown distributions.²⁹ The program combines the physical parameters of the iPEPICO experimental set up with temperature (for the initial neutral molecule internal energy distribution) and the rate constant for each pathway to calculate theoretical branching ratios for the ion dissociation as a function of photon energy, which are then compared to the experimental breakdown curves. Rice-Ramsperger-Kassel-Marcus (RRKM) theory was used to calculate $k(E)$ according to equation 1,^{35,36}

$$k(E) = \frac{\sigma N^{\ddagger}(E - E_0)}{h\rho(E)} \quad (1)$$

where σ represents the reaction degeneracy, h is Planck's constant, $N^{\ddagger}(E - E_0)$ is the number of internal states for the transition state at internal energy $(E - E_0)$ and $\rho(E)$ is the density of states for the reactant ion at internal energy (E) , and E_0 is the reaction activation energy at 0 K. For tetralin, a σ value of 4 was used for H[•]-loss corresponding to the hydrogens bound to the four sp³ carbon atoms, each CH₃[•]-loss was assigned a value of 1, C₂H₄ loss from the molecular ion was assigned $\sigma = 2$, while that from the isomer (see modeling) was assumed to be 1 and σ for C₃H₅[•]-loss was assigned a value of 1. Rotational-vibrational densities and sums-of-states were calculated using B3LYP/6-31+G(d,p) rotational constants and harmonic vibrational frequencies

by the direct count algorithm of Beyer and Swinehart.³⁷ The numbers of internal states for the transition state for the reactions were approximated using the vibrational frequencies and rotational constants of the precursor ion, less one vibrational mode to represent the reaction coordinate. Of the remaining $3N - 7$ (N = number of atoms) modes for the transition state, the lowest five frequencies were scaled to adjust the entropy of activation, $\Delta^\ddagger S$. Frequency multiplication factors less than one increase $\Delta^\ddagger S$ while values greater than one decrease $\Delta^\ddagger S$.³⁵ The agreement between the experimental and theoretical breakdown curves was achieved by varying E_0 and $\Delta^\ddagger S$. Error bars were established by finding the limits in E_0 and $\Delta^\ddagger S$ that resulted in a value of $< 5\%$ for equation 2:

$$Difference = 1 - \frac{\Sigma((Expt)(Calc))}{\sqrt{(\Sigma((Expt)(Expt))\Sigma((Calc)(Calc)))}} \quad (2)$$

where *Expt* and *Calc* refer to the experimental and calculated relative ion abundances in the breakdown curves, respectively.

RESULTS AND DISCUSSION

THRESHOLD PHOTOELECTRON SPECTRUM

The mass-selected threshold photoelectron spectrum (TPES) of tetralin was acquired from 8.3 – 15.5 eV with steps of 0.001 eV to establish the ionization energy, Fig. 1. The TPES exhibits a sharp first ionization band from which an ionization energy (IE) value of 8.46 ± 0.01 eV is derived. A simulated ionization spectrum is constructed using the program eZspectrum by considering the overlap between the vibrational wavefunctions in the ground state neutral tetralin with those in the ground state of the cation. The simulated spectrum is shown in the inset in Fig. 1 both as a stick diagram as well as a spectrum that results from a convolution of the stick diagram with

Gaussian shape with a Full-Width-at-Half-Maximum of 30 meV (250 cm^{-1}). All of the main vibronic resonances observed in the experimental spectrum are accounted for by the simulations. There is a qualitative mismatch between the measured and simulated spectrum starting at an energy of 8.6 eV which is due to an electronically-excited state in the tetralin cation. OVGf calculations were used to locate tetralin ion excited states and the results are overlaid on the TPES in Fig.1. Molecular orbital 17 produces an excited state that overlaps the ground state vibrational progression around 8.7 eV, causing the aforementioned mismatch. Tabulated molecular orbital vertical ionization energies can be found in Table S1 of supporting information.

Figure 1: Overview of the TPES of tetralin to 16 eV, with OVGf results. The inset holds an expansion of the threshold region together with a Franck-Condon simulated spectrum. The simulated spectrum is displayed both as a stick diagram, as well as a spectrum that results from a convolution of the stick spectrum with a 30 meV FWHM Gaussian line shape.

COLLISION-INDUCED DISSOCIATION (CID)

The CID breakdown graph for ionized tetralin is shown in Fig. 2.

Figure 2. CID breakdown graph for ionized tetralin.

The decomposition of tetralin leads to loss of hydrogen atoms (sequential loss of up to 4 H atoms) and hydrocarbon units ($\text{CH}_3^\bullet$, C_2H_4 and $\text{C}_3\text{H}_5^\bullet$); however, the most significant process are loss of $\text{H}^\bullet$, $\text{CH}_3^\bullet$, C_2H_4 and $\text{C}_3\text{H}_5^\bullet$ (reactions R1 – R4), the others accounting for less than 10% of the total fragmentation at high collision energy (and of this -2 H is the predominant process).

Based on the sequential appearance of the $-\text{H}^\bullet$ and $-2\text{H}^\bullet$ peaks in the breakdown graph, we conclude that $[\text{M}-2\text{H}]^{\bullet+}$ is due to a step-wise loss of two H atoms rather than loss of H_2 .

VUV-INDUCED DISSOCIATION

The major fragmentation pathways R1-R4 are also observed in the iPEPICO data (Fig. 3a), with the addition of a small peak with m/z 128 that can only be due to loss of 4 $\text{H}^\bullet$ -atoms, presumably leading to ionized naphthalene (see expanded region in Fig. S1, Supporting Information). Originally thought to be an artifact, this ion is reproducible and is also observed in the 70 eV electron ionization mass spectrum of tetralin.³⁸ The lack of this peak in the CID mass spectra, except at high collision energy after loss of three H atoms, enforces the idea that this channel in the iPEPICO experiment is possibly from a non-statistical process of the molecular ion (vide infra). The assumption that unimolecular reactions are driven by statistical dynamics is at the heart of transition state theory. So, to model the iPEPICO breakdown curves, we first removed this minor $[\text{M}-4\text{H}]^{\bullet+}$ peak (Fig. 3b). Representative time-of-flight distributions are shown in Fig. 3c.

Figure 3a) iPEPICO breakdown diagram of tetralin with $4H^\bullet$ -loss, b) RRKM (solid line) modeled iPEPICO breakdown curves ($[M-4H]^{++}$ ion removed), c) asymmetric time-of-flight distributions (with RRKM fit) at four representative photon energies. “Bin” refers to the multichannel analyzer bin number (related to the time-of-flight). The y-axis are count numbers.

RRKM MODELING

RRKM modeling of the curves in Fig. 3b,c (solid lines through the experimental points) could only be achieved by assuming a 2-well potential energy surface. This type of surface is consistent with what was required in the case of dihydronaphthalene and dihydrophenanthrene as methyl loss in those two cases required isomerization of the molecular ions to methyldiene ions (and its analogue for dihydrophenanthrene).²⁰ In addition, it was clear that there had to be two distinct sources for $[M-C_2H_4]^{++}$ and $[M-CH_3]^+$, and so the resulting, experimentally derived surface is shown in Fig. 4. The isomerization barrier governs the branching ratio between the two pathways to $[M-C_2H_4]^{++}$ and $[M-CH_3]^+$, and so the uncertainties on the reaction energies for forming these products from the isomer will be significant.

Figure 4. Two-well reaction model used for the RRKM fit to the experimental data. All energies obtained from the fitting procedure.

COMPUTATIONAL RESULTS

CH₃•-loss. The most logical source for methyl radical loss is from methylindane (**1a**, Figure 5), analogous to the loss of CH₃• from methylindene in the case of dihydronaphthalene.²⁰ We found a direct isomerization pathway from ionized tetralin (**1**) to 1-methylindane (**1a**), which then leads to the loss of a methyl radical (Figure 5). Both the isomerization energy of 2.45 eV and bond cleavage energy of 1.25 eV are consistent with those derived from the RRKM fitting of the iPEPICO data (2.24 and 1.64 eV, respectively, given the expected high uncertainty in the latter quantity).

Figure 5. Potential energy surfaces for $\text{CH}_3^\bullet$ -loss from ionized tetralin via 1-methylindane computed at the B3LYP/6-31+G(d,p) level of theory. Relative energies (eV) quoted in parentheses.

Methyl-loss directly from the tetralin molecular ion (**1**), without going through the methylindane ion **1a**, can occur via the pathway described in Fig. 6. It involves hydrogen migration prior to ring opening to form **1d**. Hydrogen migration in the newly-formed side chain can lead to the formation of allyl benzene (**4**).

Figure 6. Potential energy surfaces for $\text{CH}_3^\bullet$ -loss from ionized tetralin without participation of methylindane **1a**, computed at the B3LYP/6-31+G(d,p) level of theory. Relative energies (eV) quoted in parentheses.

C_2H_4 -loss. Unlike PAH ions which lose C_2H_2 ,^{39,40} and dihydroPAH ions which do not exhibit a 2-carbon loss channel,²⁰ tetralin starts to behave more like a regular hydrocarbon and loses C_2H_4 .³⁸

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3 It does so in two distinct channels, one from the molecular ion **1** and one from the 1-
4 methylindane isomer **1a**. A mechanism for C₂H₄-loss from the molecular ion is shown in Fig. 7
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6 and the energy required to generate the ethenylbenzene radical cation **5** is 1.40 eV. The key
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8 intermediate in this reaction, **1i**, is formed by hydrogen migration to the opposite bridging
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Figure 7. Route for C_2H_4 -loss from ionized tetralin **1** (without the participation of methylindane **1a**) at the B3LYP/6-31+G(d,p) level of theory. Relative energies (eV) quoted in parentheses. Structures **1-1h** and **1h** differ in the angle of the hydrogen atom on the bridging carbon.

C_2H_4 -loss from the 1-methylindane ion (**1a** in Figure 8) also generates ionized ethenylbenzene **5** but requires 1.99 eV (Fig. 8). This pathway is formed via a ring-opening reaction on the hydrated ring. Given the high energy of TS(**1q-1r**), it would at best be a minor contributor to the C_2H_4 -loss channel.

Figure 8. Pathway for C_2H_4 -loss from ionized 1-methylindane (calculated at the B3LYP/6-31+G(d,p) level of theory). Relative energies (eV) quoted in parentheses.

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3 Unlike naphthalene ions,⁴¹ it does not appear necessary to go through a partially hydrogenated
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5 azulene intermediate and form a dihydropentalene isomer. Three key intermediates for such a
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7 process lie 2.07, 2.01 and 2.68 eV relative to the tetralin ion (see Figure S2 in Supporting
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9 Information).

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16 **C₃H₅[•]-loss.** Two possible channels leading to the loss of the allyl radical exist. First, the loss of the
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18 allyl radical to generate the tropylium ion (**6**), the lowest energy product ion, is shown in Fig. 9.
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20 The highest barrier on this surface has an energy of 2.72 eV, significantly higher than the 2.31 eV
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22 derived from the RRKM model. Secondly, formation of the benzyl cation (**7**) requires only 2.10
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24 eV (Fig. 10), which is more consistent with the experimentally-derived value, and so this could be
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26 a case that the thermodynamically-most favoured product is not the kinetically-favoured one.
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Figure 9. Potential energy surfaces for $C_3H_5^+$ -loss to form the tropylium ion **6** from ionized tetralin, computed at the B3LYP/6-31+G(d,p) level of theory. There must be a barrier between **1n** and

products, but we were unable to optimize this structure. Relative energies (eV) quoted in parentheses.

Figure 10. Potential energy surfaces for $C_3H_5^{\bullet}$ -loss to form the benzyl cation **8** from ionized tetralin, computed at the B3LYP/6-31+G(d,p) level of theory. Relative energies (eV) quoted in parentheses.

H[•] atom loss. Simple H[•]-loss from ionized tetralin from the sp^3 carbon atoms at the 1 or 4 position has a minimum energy requirement of 1.90 eV computed at the B3LYP/6-31+G(d,p) level of theory. No reverse barrier was found from a relaxed potential energy surface scan at the B3LYP/6-31G(d) level of theory (Figure S3, Supporting Information). The energy required to remove one of the H[•] atoms from positions 2 or 3 raises to 2.56 eV, while from the unsaturated ring H loss was calculated to be 4.26 and 4.42 eV (positions 5 and 6 respectively), similar to what one expects from ionized PAHs.⁴⁰ H[•] atom loss also likely occurs from the methylindane isomer, but the low abundance of the peak in the data made it unnecessary to include a second channel in the RRKM fitting. This latter H[•]-loss reaction was calculated to have an energy requirement of 1.9 eV at the B3LYP/6-31+G(d,p) level of theory.

[M-4H]^{•+}. The products of ionized naphthalene and two H₂ molecules lie 0.93 eV above the tetralin molecular ion. The TPES in this region does not exhibit any distinctive features that would suggest a suitable candidate electronic state, Fig. 1, but the OVGF calculations place two states in the dissociation window of the [M-4H]^{•+} ion, MO 15 and 16 (Table S1). MO 15 has the opposite lobes of the orbital on adjacent C₂H₄ units, so is particularly interesting from the point of view of being able to generate two H₂ molecules (Fig. S4). This reaction would be worth exploring with an ultra-fast time-resolved spectroscopic technique.

CONCLUSIONS

Ionized tetralin, the simplest poly-hydrogenated PAH, exhibits unimolecular reactions reminiscent to those of ionized 1,2-dihydronaphthalene and cyclohexane, which has been shown also to dissociation by loss of $\text{H}^\bullet$, $\text{CH}_3^\bullet$, C_2H_4 and $\text{C}_3\text{H}_5^\bullet$ under electron- and photo-ionization.³⁸ The molecular ion can undergo isomerization by H-atom transfer and ring-opening reactions to yield $\text{H}^\bullet$, $\text{CH}_3^\bullet$, C_2H_4 and $\text{C}_3\text{H}_5^\bullet$ neutral products, the latter producing the benzyl cation rather than the lower energy tropylium ion. In addition, the molecular ion isomerizes to the 1-methylindane ion structure over a barrier of 2.24 eV (RRKM modeling) which then can go on to produce $\text{CH}_3^\bullet$ and C_2H_4 . Isomerization is dominated by facile H-atom migration to the unsaturated ring carbons. In the end, ionized tetralin does not appear to undergo facile H atom or H_2 molecule loss upon absorption of a photon, suggesting that PAHs may be sinks for H atoms in the ISM and not sources of H_2 . It will be of interest to explore larger hydrogenated PAHs to see if this is indeed a trend or unique to hydrogenated naphthalenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: . The complete citation for reference 33, Table S1 comparing experimental and OVGF orbital IEs, Figure S1 with an expanded view of the $[\text{M}-4\text{H}]^+$ region of the iPEPICO breakdown curves, Figure S2 key intermediates in the azulene-containing C_2H_4 loss mechanism, Figure S3 a potential energy scan for H loss from ionized tetraline and Figure S4 molecular orbital pictures for the lowest 8 states of ionized tetralin (PDF).

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Notes

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