THE JOURNAL OF PHYSICAL CHEMISTRY A

Photodissociation of the Cyclopentadienyl Radical at 248 nm

Mark Shapero,^{†,‡,§}[®] Isaac A. Ramphal,^{†,‡,§}[®] and Daniel M. Neumark^{*,†,‡}

[†]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States [‡]Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: The photodissociation of jet-cooled cyclopentadienyl radicals, c- C_5H_5 , at 248 nm was studied using photofragment translational spectroscopy. Two dissociation channels were observed: H + C_5H_4 and $C_3H_3 + C_2H_2$. The C_5H_4 fragment was identified as ethynylallene by its ionization energy. The translational energy distribution determined for each channel suggests that both dissociation mechanisms occur via internal conversion to the ground electronic state followed by intramolecular vibrational redistribution and dissociation. The experimental branching ratio and RRKM (Rice– Ramsperger–Kassel–Marcus) calculations favor the formation of $C_3H_3 + C_2H_2$ over the H-atom loss channel. The RRKM calculations also support the observation of ethynylallene as the dominant C_5H_4 product isomer.

$\begin{array}{c} \begin{array}{c} & H \\ & H \\$

I. INTRODUCTION

The cyclopentadienyl radical (CP), $c-C_5H_5$, is ubiquitous in hydrocarbon combustion mechanisms. The importance of CP is rooted in its stability, which allows it to accumulate in combustion environments.¹ The bimolecular reactions of CP in such environments have been studied to understand its role in polycyclic aromatic hydrocarbon (PAH) and soot formation.^{2–6} Of particular interest are the reactions of CP with acetylene,^{7–9} CP with itself,^{10–14} and CP with H atoms.^{15–17} The unimolecular decay of CP is also of interest in combustion but has only been minimally investigated despite the prevalence of this species. This work aims to probe the decomposition of CP by studying its photodissociation after excitation at 248 nm.

Spectroscopic studies of CP have focused on elucidating the nature of its $\tilde{X} \, {}^{2}E_{1}''$ ground state and associated vibronic coupling. ${}^{18-21}$ Initial condensed-phase electron paramagnetic resonance (EPR) spectroscopy suggested a permanent structural distortion owing to Jahn–Teller (JT) coupling. ${}^{22-24}$ Miller and co-workers have investigated JT effects in the ground state via laser-induced fluorescence from the electronically excited $\tilde{A} \, {}^{2}A_{2}''$ state, finding that JT distortion is dynamic rather than static. ${}^{25-29}$ Further spectroscopic investigations of CP have been carried out using ultrafast electron diffraction, 30 anion photoelectron spectroscopy, 31 and IR spectroscopy in a cryogenic matrix 32 and in He droplets. 33

The thermal decomposition of CP has been studied only as a secondary reaction from the shock tube pyrolysis of cyclopentadiene.^{34–36} Burcat and Dvinyaninov³⁴ measured the pyrolysis products using a gas chromatograph and flame ionization detector, Kern et al.³⁵ detected products by time-of-flight mass spectrometry, and Roy et al.³⁶ used absorption spectroscopy to measure both H atom and acetylene time

profiles. All three investigations proposed that CP decomposed solely to the propargyl radical, C_3H_3 , and acetylene, C_2H_2 , in a three-step process beginning with a 1,2-hydrogen shift followed by ring-opening and ending with dissociation. These previous techniques cannot distinguish between primary CP decomposition products, secondary decomposition products, or non-unimolecular reaction products. Other experiments have explored the role of C_3H_5 in the bimolecular reactions of $C_2H + CH_3CCH$, $C_2H + H_2CCCH_2$, and $C_2H_2 + C_3H_3$.^{37–39}

No photodissociation or absorption experiments have been carried out on CP near 248 nm,¹⁸ but our calculations (see Section III) suggest that there is a weak transition at 247 nm (5.02 eV). There have been few previous theoretical discussions regarding the existence or nature of excited states at this energy. The earliest work used semiempirical molecular orbital (MO) treatments that resulted in poor agreement with the experimentally observed transition energy of ~3.7 eV.^{40,41} A more sophisticated CNDO-SCF-CI calculation gave an energy for the $\tilde{A} {}^{2}A_{2}^{"} \leftarrow \tilde{X} {}^{2}E_{1}^{"}$ transition in excellent agreement with previous experimental findings.⁴² This CI calculation also found states at 4.94 eV (${}^{2}E_{1}^{"} \leftarrow {}^{2}E_{1}^{"}$), 5.13 eV (${}^{2}E_{2}^{'} \leftarrow {}^{2}E_{1}^{"}$), and 5.29 eV (${}^{2}E_{1}^{'} \leftarrow {}^{2}E_{1}^{"}$).

In-depth theoretical calculations of CP decomposition were first reported by Moskaleva and Lin,⁴³ who only considered the pathway to the propargyl radical and acetylene. A more complete potential energy diagram was reported recently by Jamal and Mebel⁴⁴ that includes additional decomposition products. A simplified potential energy diagram is shown in

```
Received:November 30, 2017Revised:February 14, 2018Published:February 16, 2018
```

ACS Publications © 2018 American Chemical Society



Figure 1. A simplified C_5H_5 potential energy diagram showing the production of propargyl + acetylene, ethynylallene + H, 1,4-pentadiyne + H, and diacetylene + methyl. The energetics and pathways are compiled from refs 43–45. All energies are in kcal/mol.

Figure 1. All pathways begin with a 1,2-hydrogen shift forming the 1,3-cyclopentadien-4-yl radical (W2). This intermediate then ring-opens and, depending on which bond breaks, forms either the 1,3,4-pentatrienyl radical (W3), or the 1-penten-4ynyl radical (W4). The cyclic intermediate can also form 1,3cyclopentadien-3-yl radical (W5) that can ring-open to form vinylpropargyl radical (VP, W6).45 From these ring-opened species there are many reaction possibilities, including direct dissociation pathways to form the propargyl radical and acetylene (P1) as well as hydrogen atom loss to form ethynylallene (P2) or 1,4-pentadiyne (P3). Additional isomerization and dissociation channels exist, with products including H, CH₃, C₂H, C₃H₄, C₄H₂, and C₅H₄; see ref 44 for more details. Direct hydrogen atom loss from CP is possible without intervening isomerization, but it has a large energy barrier and thus is not expected to play an important role in thermal decomposition.⁴⁴ The channels of interest in this work are⁴⁴

$$CP \rightarrow C_3H_3 + C_2H_2 \quad \Delta H_{0K} = 74.1 \text{ kcal/mol}$$
(1)

 \rightarrow ethynylallene + H $\Delta H_{0K} = 91.0 \text{ kcal/mol}$ (2)

 \rightarrow 1,4-pentadiyne + H $\Delta H_{0K} = 95.5 \text{ kcal/mol}$ (3)

$$\rightarrow$$
 methyl + diacetylene $\Delta H_{0K} = 78.7 \text{ kcal/mol}$ (4)

To gain additional insights into the unimolecular decay of the cyclopentadienyl radical, we investigated its collisionless ultraviolet photodissociation dynamics at 248 nm using molecular beam photofragment translational spectroscopy. This experiment can in principle detect all channels and thus assess their existence and relative importance. Both channels 1 and 2 are observed. The translational energy distributions determined for each channel suggest internal conversion to the ground electronic state followed by statistical decay. The branching ratio between the observed channels is determined and compared to RRKM calculations: both experiment and the RRKM treatment find channel 1 to be dominant.

II. EXPERIMENTAL SECTION

Cyclopentadienyl radical photodissociation was studied on a modified crossed molecular beam apparatus with a fixed source and rotatable detector as described previously.^{46–48} A pulsed CP beam was produced by flash pyrolysis of anisole as it passed through a resistively heated SiC tube attached to the nozzle of a piezoelectric pulsed valve.^{49–51} Anisole decomposes to CP via a two-step mechanism, first losing a methyl group and then undergoing ring contraction with the loss of CO to form CP.^{52,S3}

The pulsed valve was backed with a gas mixture of 1.2 atm of 10% N₂ in He bubbled through an ice-water cooled sample of anisole (Fluka, >99%). The molecular beam was collimated with two skimmers that separate the source chamber from the main scattering chamber. The collimated beam was crossed at 90° by a focused, unpolarized laser pulse with a fluence of 400 mJ/cm² at 248 nm from an LPX 220i excimer laser. The pulsed valve and laser were operated at 400 and 200 Hz, respectively, which allowed for background subtraction from the radical beam. The scattered photofragments were detected as a function of laboratory angle, Θ_{Lab} , in the plane defined by the laser and the molecular beam. After passing into a triply differentially pumped detector, the photofragments were ionized via electron impact ionization with 80 eV electrons. The resulting ions were mass-selected with a quadrupole mass filter and detected with a Daly style ion detector.⁵⁴ The ion signal as a function of time relative to the laser pulse was acquired with a multichannel scalar interfaced with a computer for 1×10^5 to 2×10^6 laser shots. The time-of-flight (TOF) spectra were simulated using a forward convolution method to iteratively determine the center-of-mass translational energy distributions for each product channel.

Mass spectra of the molecular beam were used to verify anisole depletion (m/z = 108) and CP formation (m/z = 65); examples are shown in Figure 2. The upper trace is the precursor mass spectrum taken with pyrolysis off; the parent peak is visible at m/z = 108. With pyrolysis on, the parent peak disappears and the resulting mass spectrum (lower trace) is

The Journal of Physical Chemistry A



Figure 2. Mass spectra of the molecular beam normalized to the signal intensity at m/z = 65: (a) pyrolysis off; (b) pyrolysis on. The peak at m/z = 108 disappears with pyrolysis on, indicating depletion of the precursor.

dominated by the CP parent mass. Because of dissociative ionization, there is a daughter peak at m/z = 65 from the precursor molecule in the upper trace of Figure 2. However, once the m/z = 108 peak is depleted, it is expected that the m/z = 65 peak comes mainly from CP.

Further confirmation of CP formation is shown by the ionization efficiency curves for m/z = 65 in Figure 3. The signal



Figure 3. Ionization efficiency curves of m/z = 65 with pyrolysis off and on. The appearance potential for this signal with pyrolysis off is 14.6 eV, whereas with pyrolysis on, it is 8.7 eV.

intensity at m/z = 65 was measured as the electron ionization energy was varied from 5 up to 20 eV while keeping the emission current constant. The energy scale was calibrated by the ionization of N₂ in the molecular beam. The appearance energy is the extrapolated intercept from the linear region of the curve. The appearance energy for signal at m/z = 65 with pyrolysis off is 14.6 eV, which indicates it is due to dissociative ionization, while with pyrolysis on, the appearance energy of 8.7 eV matches the known ionization energy of 8.6 eV for CP.⁵⁵ Other C₃H₅ isomers typically have lower ionization potentials (e.g., VP, 7.9 eV).^{56,57}

The CP beam velocity was characterized with a spinning slotted chopper wheel. Typical beam velocities were around 2000 m/s with speed ratios, defined as the beam flow velocity divided by the velocity spread, in the range of 3-5.

III. THEORETICAL CALCULATIONS

Electronic Structure. The ground-state geometry reported in ref 43 was used as the input to search for excited states of Article

CP. Time-dependent density functional theory (TD-DFT) using the ω B97X-D functional and the 6-311++(d, p) basis set was used to identify excited states of CP. A weak transition was identified at 5.02 eV (247 nm, f = 0.0002), corresponding to a $\sigma \rightarrow \pi^*$ transition. The low oscillator strengths calculated here and in ref 42 may account for this feature not being observed in the spectrum collected by Thrush.¹⁸ For comparison, the next lowest-energy isomer in Figure 1 is VP, which has three transitions near 248 nm, occurring at 263 nm (f = 0.1764), 251 nm (f = 0.0003), and 238 nm (f = 0.3222).

RRKM. Rice-Ramsperger-Kassel-Marcus (RRKM) calculations of dissociation rates were performed as points of comparison to various experimental observations. The stationary points of interest are depicted on the potential energy diagram in Figure 1 and are collected from refs 43-45. The densities and sums of states for each local minimum and transition state were calculated using the Beyer-Swinehart algorithm⁵⁸ with the reported energies and vibrational frequencies treated as harmonic oscillator frequencies. Internal rotations in W3, W4, W8, TS7, TSA, TSB, TSC, TSD, TSE, and TSF were treated as free rotors in calculating the densities and sums of states.⁵⁹ Individual rate constants were calculated using the microcanonical RRKM equation. The maximum energy was given by the photon energy (115 kcal/mol). No tunneling effects were considered. All reaction pathways shown in Figure 1 were considered, using the steady-state approximation on the intermediate local minima to solve for the relative rates for each channel.

IV. RESULTS

On the basis of our expectation that channels 1-4 are the main dissociation channels, TOF spectra were taken at parent m/z values for these channels (m/z = 64, 50, 39, 26, and 15) and for several other m/z values that could result from dissociative ionization (DI) of these parent species.

Time-of-flight spectra were measured at m/z = 64, $C_5H_4^+$, at laboratory angles $\Theta_{Lab} = 3^\circ$, 4° , 5° , 6° , 7° , 8° , and 10° with respect to the molecular beam axis. Selected small-angle TOF spectra are shown as open circles in Figure 4. The TOF spectra



Figure 4. Representative TOF spectra of m/z = 64 at 3°, 4°, and 5°. The open circles are data points, and the blue line is a simulation based on the blue $P(E_T)$ distribution in Figure 8. Signal is normalized to counts per 10⁵ laser shots.

at m/z = 64 below $\Theta_{\text{Lab}} = 6^{\circ}$ comprise only a single dominant feature. Beyond $\Theta_{\text{Lab}} = 6^{\circ}$ there is a faster, less intense feature that extends past where CP H-atom loss can occur (Figure S1). The m/z = 64 species was further characterized by measurement of its ionization efficiency curve at $\Theta_{\text{Lab}} = 4^{\circ}$ shown in Figure 5. The on-axis m/z = 64 signal with an appearance energy of 13.6 eV is due to the dissociative ionization of CP. The off-axis m/z = 64 signal comes from the ionized parent fragment of the photodissociation of CP, and the appearance



Figure 5. Ionization efficiency curves of m/z = 64 on and off of the molecular beam axis. The off-axis signal was measured at $\Theta_{\text{Lab}} = 4^\circ$. The appearance potential for the signal on axis is 13.6 eV, whereas off axis it is 9.4 eV.

energy of 9.4 eV matches the ionization energy of 9.2 eV for ethynylallene, the heavier fragment from channel 2.⁵⁷ The other potential fragment with parent ion signal at m/z = 64, 1,4-pentadiyne, has an ionization energy of 10.3 eV.⁵⁷

TOF spectra at m/z = 39, $C_3H_3^+$, and m/z = 26, $C_2H_2^+$, were detected at laboratory angles ranging from $\Theta_{Lab} = 4^\circ$ up to 30°. Representative spectra are shown in Figure 6. If these signals



Figure 6. Representative TOF spectra of m/z = 39 and 26. The data are shown as open circles. The solid lines are simulations based on the $P(E_T)$ distribution in Figure 9; the red line is from C_3H_3 and the orange line from C_2H_2 . Both fragments contribute to the m/z = 26 simulation; the total simulated signal is indicated by the black line. Signal is normalized to counts per 10^5 laser shots.

indeed correspond to channel 1, it should be possible to simulate them with the same photofragment translational energy distribution; i.e., they are "momentum-matched", as discussed in more detail in section V.

Investigation of channel 4 was conducted at m/z = 50 and 15. TOF spectra at m/z = 50 were essentially identical to the m/z = 64 spectra, indicating that the m/z = 50 signal was from dissociative ionization of C_5H_4 . Attempts to detect signal at m/z = 15 were unsuccessful.

Figure 7 shows TOF spectra taken at $\Theta_{\text{Lab}} = 4^{\circ}$ for ion signals with m/z = 24 and 25. These signals can result from DI of the products from channels 1–3. As such, they are used to determine the product branching ratio as discussed in section V.



Figure 7. TOF spectra of m/z = 24 and 25 collected at 4°. The data are shown as open circles. The black line is the summed simulation, which has three components: the orange and red lines are from the C_2H_2 and C_3H_3 components, respectively, of the $P(E_T)$ distribution in Figure 9, and the blue line comes from the blue C_5H_4 component of the $P(E_T)$ distribution in Figure 8. Both spectra were taken for 2×10^6 laser shots.

Other sources of signal besides CP photodissociation were considered in light of the high-angle signal at m/z = 64. It is conceivable that there is a small contribution to our TOF spectra from the photodissociation of the radical precursor, anisole, since it is not completely depleted in the molecular beam. From photodissociation studies of anisole with the pyrolysis source off, the dominant signal appears at m/z = 65. With pyrolysis on, the dominant signal occurs at m/z = 64, and there is very little signal at m/z = 65 off the beam axis. Higher than expected counts at m/z = 92 in the molecular beam during pyrolysis may be due to formation of 6-fulvenone through a minor fragmentation pathway of anisole, although the barriers to forming this species are substantial compared to those leading to CP + CO.⁶⁰ Furthermore, irradiation of matrixisolated 6-fulvenone with 254 ± 10 nm did not lead to measurable loss of CO that would yield m/z = 64.⁶¹ The most plausible explanation for the fast m/z = 64 signal in Figure S1 is from photodissociation of small amounts of other C5H5 isomers, produced either by isomerization of CP in the pyrolysis source or direct formation from anisole pyrolysis. There is a relatively low-energy isomerization pathway to the vinylpropargyl radical (W6, Figure 1), but other isomers are also possible. Dissociation of VP or higher-energy isomers would lead to more energy available to the C_5H_4 fragments formed by H-atom loss, which could produce signal at larger scattering angles.

Possible contributions from two photon processes were assessed by conducting a laser power dependence study. TOF spectra taken over the range of $33-667 \text{ mJ/cm}^2$ showed a linear signal intensity dependence on laser power and no qualitative differences in the shape of the TOF spectra.

V. ANALYSIS

The TOF spectra and off-axis ionization data in the previous section suggest that CP photodissociation results in channels 1 and 2 and possibly channel 3. In this section, we use kinematic analysis to confirm that these channels are present and characterize them through their center-of-mass (CM) translational energy distributions.

Conservation of energy in this experiment is expressed by

$$E_{\text{avail}} = h\nu + E_0 - D_0 = E_{\text{int}} + E_{\text{T}}$$
 (I)

The available energy to the photoproducts, E_{availb} is the sum of the photon energy, $h\nu$, and any initial internal energy, E_0 , minus the dissociation energy, D_0 , for the specific channel. This available energy can be partitioned into either the internal energy, E_{intb} or the relative translational energy, E_{T} , of the fragments. The initial internal energy of CP following supersonic jet expansion is unknown but is approximated as zero for the purposes of analysis, which is supported by our previous work on phenyl radical expansions seeded in He with $10\% N_2$.⁶²

When all of the available energy is partitioned into translational energy, the maximum laboratory scattering angle for each photofragment can be calculated with knowledge of the CP beam velocity. Kinematic analysis shows that for channel 2, the m/z = 64 ethynylallene fragment cannot scatter beyond $\Theta_{\text{Lab}} = 6^\circ$, based on the radius of the Newton circle for this channel.⁶³ The m/z = 1 counter fragment for channels 2 and 3 is kinematically allowed at all laboratory angles, which combined with high detector background at m/z = 1, short residence time in the ionization region, and small ionization cross section prohibited its detection.

Signals at m/z = 26 and 39 are present beyond where m/z = 64 was detected and therefore cannot be due to the dissociative ionization of C₅H₄. Further, the parent ions at m/z = 26 and 39 from channel 1 are kinematically allowed at all measurable laboratory angles, and these fragments were detected at all laboratory angles out to $\Theta_{\text{Lab}} = 30^{\circ}$.

The photofragment TOF spectra are governed by the centerof-mass angular and translational energy distribution, $P(E_T, \theta)$. The total distribution can be uncoupled to yield

$$P(E_{\rm T},\,\theta) = P(E_{\rm T}) \times I(\theta,\,E_{\rm T}) \tag{II}$$

where $P(E_{\rm T})$ is the center-of-mass translational energy distribution and $I(\theta, E_{\rm T})$ is the center-of-mass angular distribution. The TOF spectra are analyzed using PHO-TRAN,⁶⁴ a forward convolution program that simulates the TOF spectra given the center-of-mass angular and translational energy distributions. An initial guess of the $P(E_{\rm T})$ distribution is iteratively adjusted until good agreement is reached between the data and the simulation. The analysis assumes that CP photodissociation is isotropic, which results in an adequate simulation of the present data.

Figure 8 shows the $P(E_T)$ distribution for H atom loss. The black curve fits the entire data set at m/z = 64. This distribution



Figure 8. Center-of-mass $P(E_T)$ distribution for m/z = 64 photofragments (black). This distribution is separated into a blue distribution for cyclopentadienyl photodissociation to $C_5H_4 + H$ and a green distribution representing signal contamination by other molecules in the beam. The available energy for C_5H_4 from CP dissociation is 24 kcal/mol, indicated by a blue arrow.

drops to nearly zero for $E_{\rm T} \ge 30$ kcal/mol but has a weak tail extending to 72 kcal/mol, well beyond the maximum allowed value of $E_{\rm T} = 24$ kcal/mol for channel 2. This distribution is separated into a blue distribution that simulates CP H-atom loss for $\Theta_{\rm Lab} \le 6^{\circ}$, and a green distribution that simulates the

high-angle m/z = 64 TOF spectra. The resulting TOF simulations for CP H-atom loss are shown as blue lines in Figure 4. For the blue distribution, the peak energy is 5 kcal/ mol with $\langle E_{\rm T} \rangle = 8$ kcal/mol and $E_{\rm T,max}$ set to 24 kcal/mol to agree with the available energy for channel 2. The average fraction of energy that goes into translation for this distribution is $\langle f_{\rm T} \rangle = 0.33$. The green distribution that simulates the highangle m/z = 64 signal (Figure S1) is attributed to photodissociation from C₅H₅ species other than CP in the molecular beam; possible sources were discussed in Section IV. TOF spectra at m/z = 64 collected with low electron impact ionization energy (15 eV) did not appear different from the 80 eV TOF spectra. The shape of this feature also did not appear to vary with changes in laser fluence, laser polarization angle, or temperature in the pyrolysis source.

The $P(E_{\rm T})$ distribution for channel 1 is shown in Figure 9 with the resulting simulations of both m/z = 39 and 26 shown



Figure 9. Center-of-mass $P(E_T)$ distribution for cyclopentadienyl photodissociation to $C_3H_3 + C_2H_2$.

as solid lines in Figure 6. It is peaked at 8 kcal/mol with $\langle E_{\rm T} \rangle =$ 10 kcal/mol and $\langle f_{\rm T} \rangle =$ 0.24. The $P(E_{\rm T})$ distribution extends to a maximum translational energy of 33 kcal/mol, which is within the available energy of 40.9 kcal/mol for this channel. We find that the TOF spectra for both fragments can be simulated by the same $P(E_{\rm T})$ distribution. This is a signature of "momentum matching"; that is, the two fragments are formed with equal and opposite momenta as required if they originate from the same dissociation event. This observation thus supports the assignment of these features to channel 1. The weighting of each fragment in the simulation of the m/z = 26 TOF spectra in Figure 6 is set so the branching ratio between C₃H₃ and C₂H₂ is unity as calculated from rearranging eq III and solving for the weightings.

Because of extensive dissociative ionization that occurs from electron impact ionization at 80 eV, there is signal from m/zvalues that have components from both H atom loss and C_3H_3 + C_2H_2 . TOF spectra at these m/z values are useful for estimating the branching ratio between these channels. Within $\Theta_{Lab} = 6^\circ$, where signal from channels 1 and 2 can occur, the photodissociation signal at m/z = 24 and 25 cannot be well simulated by either $P(E_T)$ alone; components from both channels are required for the spectra to be well-simulated. Figure 7 shows TOF spectra at m/z = 24 and 25 with the total simulation in the black line and components from each dissociation pathway as blue, red, and orange lines.

The branching ratio (BR) between the two pathways can be calculated using eq III.

$$= \frac{W_{\rm CH1}}{W_{\rm CH2+3}} \times \frac{\sigma_{\rm C_{5}H_{4}}}{\sigma_{\rm C_{3}H_{3} \text{ or } \rm C_{2}H_{2}}} \times \frac{f_{\rm C_{5}H_{4}}}{f_{\rm C_{3}H_{3} \text{ or } \rm C_{2}H_{2}}}$$
(III)

The weighting of each $P(E_{\rm T})$, W_{ν} in the TOF simulation was determined by matching the total simulation to the data. This weighting was then normalized by the ionization cross section, σ_{ii} of the parent fragment estimated by the scheme of Fitch and Sauter⁶⁵ and by f_{ii} the probability that each parent fragment will dissociatively ionize to m/z = 24 or 25. For the C₅H₄ fragment, this probability was determined by collecting signal at $\Theta_{Lab} = 6^{\circ}$ for all m/z values with measurable signal intensity (64, 63, 62, 61, 60, 52, 51, 50, 49, 48, 39, 38, 37, 36, 26, 25, and 24). The integrated signal that was simulated by the blue $P(E_{\rm T})$ distribution from Figure 8 was used to determine the dissociative ionization pattern of the C5H4 fragment, which is reported in Figure S2. The acetylene fragmentation pattern was taken from NIST,66 and the propargyl fragmentation pattern was calculated in a previous study on this apparatus.^{67,68} Taking all of these factors into account, the m/z = 24 and 25 TOF spectra at $\Theta_{Lab} = 4^{\circ}$ yield the experimental branching ratio of channel 1:channel 2 + 3 is 64%:36%.

The branching ratio calculated using eq III can be compared with the results given by the RRKM calculation that represents the statistical ground state dissociation mechanism. All calculated rate constants are below $1 \times 10^{11} \text{ s}^{-1}$, which should allow enough time for vibrational energy redistribution. The RRKM analysis predicts the branching ratio of channel 1:channel 2 + 3 is 92%:8%. The statistical branching ratios between the other channels were also calculated. For the two H atom loss pathways, the ratio is 97% channel 2:3% channel 3, and the channel 1:channel 4 ratio is 99.999%:0.001%. Hence, both experiment and theory predict channel 1 to be the dominant pathway, followed by channel 2, but less of channel 2 is predicted by the RRKM calculations than is seen experimentally. This discrepancy is considered further in Section VI.

VI. DISCUSSION

The goal of this study was to assess how the cyclopentadienyl radical, CP, photodissociates after excitation at 248 nm in a collisionless environment with interest in identifying the photofragments and the dissociation mechanism. Results suggest that there are two competing pathways: an H atom loss pathway and an acetylene + propargyl pathway.

The existence of an H atom loss channel from CP was previously inferred from bimolecular reactions on the C_5H_5 potential energy surface but was never measured directly from CP.³⁸ The fragment measured in this experiment at m/z = 64 was identified as ethynylallene by the agreement with its ionization energy. This identification is further supported by RRKM calculations that predict ethynylallene as the dominant C_5H_4 product from CP dissociation. The production of ethynylallene is assigned to H-atom loss channel 2 from CP.

Although the acetylene and propargyl channel dominates the literature for CP decomposition, only the acetylene fragment has been previously detected from the secondary decomposition of cyclopentadiene. In this experiment, both m/z = 39 and m/z = 26 were measured, and since the TOF spectra at both m/z values were simulated by the respective fragments of the $P(E_T)$ distribution in Figure 9, they come from the same dissociation event of CP. Furthermore, the maximum transla-

tional energy in the $P(E_T)$ distribution of Figure 9 agrees with the energetic constraints for channel 1.

Channel 4, methyl + diacetylene, has a lower asymptotic energy than both H atom loss pathways,⁴⁴ but the pathway to its formation has more steps with higher and more constrained barriers compared to the other channels. The lack of signal from this channel is supported by the RRKM calculation, which suggests that this channel should account for much less than 1% of the total dissociation.

The nature of the $P(E_T)$ distributions in Figures 8 and 9 suggest that the dissociation mechanisms for channels 1 and 2 involve internal conversion to the ground electronic state followed by energy randomization and dissociation over a barrier. The peak positions in Figures 8 and 9 are shifted away from 0 kcal/mol, which is indicative of exit barriers on the potential energy surface. From Figure 1, there are exit barriers of 15.6 and 6.8 kcal/mol for channels 1 and 2, respectively. These are reflected in the $P(E_T)$ distributions where the larger exit barrier corresponds to a peak at higher translational energy; the peaks positions are 8 and 5 kcal/mol in the $P(E_T)$ distributions corresponding to channels 1 and 2, respectively.

If internal conversion to the ground state is followed by rapid intramolecular vibrational redistribution of energy, then the experimental branching ratios should be similar to those calculated by RRKM. While both the experimental and calculated branching ratios favor channel 1 and find channel 2 to be the only other significant reaction, the experimentally determined amount of channel 2 is higher than the calculated value. This disagreement would be mitigated if some of the $C_{\rm S}H_4$ signal seen here were from dissociation of another molecule in the radical beam.

As discussed in Section IV, it is possible that a higher-energy isomer of CP such as VP is generated in the flash pyrolysis source, either by isomerization of CP or as a by-product in the pyrolysis of anisole.⁴⁵ Photodissociation of VP would yield higher-energy H atoms and could thus be responsible for the green contribution to the $P(E_T)$ distribution in Figure 8; the maximum value of E_T for H atom loss from VP is 54 kcal/mol, covering most (but not all) of this distribution. RRKM calculations for VP yield a channel 1:channel 2 branching ratio of 49%:51%, so the presence of VP can increase the overall experimental contribution from channel 2.

We believe the radical beam contains predominantly CP given the excellent agreement between the known IP and the measured appearance potential for m/z = 65. However, given the small oscillator strength calculated for CP, it is possible that isomers such as VP (Section III) with stronger absorption near 248 nm contribute disproportionately to our signal despite their low abundance. Photodissociation of these species could thus affect the $P(E_T)$ distribution needed to fit the data and skew the experimental branching ratio in favor of H atom loss, leading to disagreement with the RRKM calculations.

Unfortunately, we have no way to assess to what extent such species might be present in our experiment. It would be of interest to study this channel further on an apparatus that can detect H atoms, 69,70 to test if the higher-energy C₅H₄ signal is mirrored in the kinetic energy distribution of the H atoms.

VII. CONCLUSIONS

Photodissociation of the cyclopentadienyl radical was studied upon excitation at 248 nm. There is evidence that supports two dissociation channels: $C_5H_4 + H$, with the C_5H_4 fragment being ethynylallene, and $C_3H_3 + C_2H_2$. Both dissociation channels are

The Journal of Physical Chemistry A

attributed to internal conversion to the ground state followed by intramolecular vibrational energy redistribution and dissociation. This mechanism is supported by the shape of each $P(E_T)$ distribution. The experimental branching ratio and RRKM calculations favor the formation of $C_3H_3 + C_2H_2$ over the H atom loss channel, but more H atom loss is seen in the experiment than is predicted by the calculations for cyclopentadienyl dissociation, and higher-energy C_5H_4 fragments are present than can be formed from CP alone. These observations are attributed to the minor presence of higher-energy C_5H_5 isomers in the radical beam.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b11837.

Additional TOF spectra for m/z = 64, and a fragmentation pattern for the mass 64 photofragment (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: dneumark@berkeley.edu.

ORCID 0

Mark Shapero: 0000-0003-3082-0547

Isaac A. Ramphal: 0000-0002-6102-2065

Author Contributions

[§]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Dr. Gabriel da Silva for helpful discussions. This work was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences division of the U.S. Department of Energy under Contract DE-AC02-05CH11231. I.A.R. acknowledges support from the Klaus and Mary Ann Saegebarth Fellowship.

REFERENCES

(1) Butler, R. G.; Glassman, I. Cyclopentadiene combustion in a plug flow reactor near 1150K. *Proc. Combust. Inst.* **2009**, 32 (1), 395–402.

(2) Wang, D.; Violi, A. Radical-molecule reactions for aromatic growth: a case study for cyclopentadienyl and acenaphthylene. *J. Org. Chem.* **2006**, *71* (22), 8365–8371.

(3) Wang, D.; Violi, A.; Kim, D. H.; Mullholland, J. A. Formation of naphthalene, indene, and benzene from cyclopentadiene Pyrolysis: a DFT study. *J. Phys. Chem. A* **2006**, *110* (14), 4719–4725.

(4) Cavallotti, C.; Polino, D.; Frassoldati, A.; Ranzi, E. Analysis of some reaction pathways active during cyclopentadiene pyrolysis. *J. Phys. Chem. A* **2012**, *116* (13), 3313–3324.

(5) Comandini, A.; Brezinsky, K. Radical/ π -bond addition between o-benzyne and cyclic C5 hydrocarbons. *J. Phys. Chem. A* **2012**, *116* (4), 1183–1190.

(6) Xu, F.; Shi, X.; Zhang, Q.; Wang, W. Mechanism for the growth of polycyclic aromatic hydrocarbons from the reactions of naphthalene with cyclopentadienyl and indenyl. *Chemosphere* **2016**, *162*, 345–354.

(7) Fascella, S.; Cavallotti, C.; Rota, R.; Carrà, S. The Peculiar kinetics of the reaction between acetylene and the cyclopentadienyl radical. *J. Phys. Chem. A* **2005**, *109* (33), 7546–7557.

(8) Cavallotti, C.; Mancarella, S.; Rota, R.; Carrà, S. Conversion of C5 into C6 cyclic species through the formation of C7 intermediates. *J. Phys. Chem. A* **2007**, *111* (19), 3959–3969.

(9) da Silva, G.; Cole, J. A.; Bozzelli, J. W. Kinetics of the cyclopentadienyl + acetylene, fulvenallene + H, and 1-ethynylcyclopentadiene + H reactions. J. Phys. Chem. A **2010**, 114 (6), 2275–2283. (10) Melius, C. F.; Colvin, M. E.; Marinov, N. M.; Pit, W. J.; Senkan, S. M. Reaction mechanisms in aromatic hydrocarbon formation involving the C_5H_5 cyclopentadienyl moiety. Symp. (Int.) Combust,

[Proc.] **1996**, 26 (1), 685–692. (11) Filley, J.; McKinnon, J. T. Dimerization of cyclopentadienyl radical to produce naphthalene. *Combust. Flame* **2001**, *124* (4), 721–723

(12) Mebel, A. M.; Kislov, V. V. Can the $C_5H_5 + C_5H_5 \rightarrow C_{10}H_{10} \rightarrow C_{10}H_9 + H/C_{10}H_8 + H_2$ reaction produce naphthalene? An ab initio/ RRKM study. *J. Phys. Chem. A* **2009**, *113* (36), 9825–9833.

(13) Cavallotti, C.; Polino, D. On the kinetics of the $C_5H_5+C_5H_5$ reaction. *Proc. Combust. Inst.* 2013, 34 (1), 557–564.

(14) Knyazev, V. D.; Popov, K. V. Kinetics of the self reaction of cyclopentadienyl radicals. *J. Phys. Chem. A* 2015, 119 (28), 7418–7429.

(15) Zhong, X.; Bozzelli, J. W. Thermochemical and kinetic analysis of the H, OH, HO₂, O, and O₂ association reactions with cyclopentadienyl radical. *J. Phys. Chem. A* **1998**, *102* (20), 3537–3555.

(16) Roy, K.; Braun-Unkhoff, M.; Frank, P.; Just, T. Kinetics of the cyclopentadiene decay and the recombination of cyclopentadienyl radicals with H-atoms: Enthalpy of formation of the cyclopentadienyl radical. *Int. J. Chem. Kinet.* **2001**, 33 (12), 821–833.

(17) Harding, L. B.; Klippenstein, S. J.; Georgievskii, Y. On the combination reactions of hydrogen atoms with resonance-stabilized hydrocarbon radicals. *J. Phys. Chem. A* **2007**, *111* (19), 3789–3801.

(18) Thrush, B. A. Spectrum of the cyclopentadienyl radical. *Nature* **1956**, *178*, 155–156.

(19) Porter, G.; Ward, B. Photolytic preparation of cyclopentadienyl and phenyl nitrene from benzene derivatives. *Proc. R. Soc. London, Ser. A* **1968**, 303, 139–156.

(20) Engleman, R., Jr.; Ramsay, D. A. Electronic absorption spectrum of cyclopentadienyl radical (C_5H_5) and its deuterated derivatives. *Can. J. Phys.* **1970**, *48* (8), 964–969.

(21) Kiefer, J. H.; Tranter, R. S.; Wang, H.; Wagner, A. F. Thermodynamic functions for the cyclopentadienyl radical: The effect of Jahn–Teller distortion. *Int. J. Chem. Kinet.* **2001**, 33 (12), 834–845. (22) Liebling, G. R.; McConnell, H. M. Study of molecular orbital

degeneracy in C_5H_5 . J. Chem. Phys. **1965**, 42 (11), 3931–3934.

(23) Hedaya, E. Techniques of flash vacuum pyrolysis. Cyclopentadienyl radical and its dimer. *Acc. Chem. Res.* **1969**, *2* (12), 367– 373.

(24) Kira, M.; Watanabe, M.; Sakurai, H. Chemistry of organosilicon compounds. 100. Substituent effects on the electron spin resonance spectra of cyclopentadienyl radicals. Removal of degeneracy by organosilyl groups. J. Am. Chem. Soc. **1977**, *99* (24), 7780–7785.

(25) Heaven, M.; Dimauro, L.; Miller, T. A. Laser-induced fluorescence spectra of free-jet cooled organic free radicals. Vinoxy, cyclopentadienyl, and benzyl. *Chem. Phys. Lett.* **1983**, 95 (4), 347–351.

(26) Yu, L.; Foster, S. C.; Williamson, J. M.; Heaven, M. C.; Miller, T. A. Rotationally resolved electronic spectrum of jet-cooled cyclopentadienyl radical. *J. Phys. Chem.* **1988**, *92* (15), 4263–4266.

(27) Yu, L.; Williamson, J. M.; Miller, T. A. Rotationally resolved electronic spectrum of jet-cooled deuterated cyclopentadienyl radical. *Chem. Phys. Lett.* **1989**, *162* (6), 431–436.

(28) Applegate, B. E.; Miller, T. A.; Barckholtz, T. A. The Jahn– Teller and related effects in the cyclopentadienyl radical. I. The ab initio calculation of spectroscopically observable parameters. *J. Chem. Phys.* **2001**, *114* (11), 4855–4868.

(29) Applegate, B. E.; Bezant, A. J.; Miller, T. A. The Jahn–Teller and related effects in the cyclopentadienyl radical. II. Vibrational analysis of the $\tilde{A} {}^{2}A_{2}'' - \tilde{X} {}^{2}E_{1}''$ electronic transition. *J. Chem. Phys.* **2001**, *114* (11), 4869–4882.

(30) Ihee, H.; Feenstra, J. S.; Cao, J.; Zewail, A. H. Ultrafast electron diffraction of transient cyclopentadienyl radical: A dynamic pseudorotary structure. *Chem. Phys. Lett.* **2002**, 353 (5), 325–334.

The Journal of Physical Chemistry A

(31) Ichino, T.; Wren, S. W.; Vogelhuber, K. M.; Gianola, A. J.; Lineberger, W. C.; Stanton, J. F. The vibronic level structure of the cyclopentadienyl radical. *J. Chem. Phys.* **2008**, *129* (8), 084310.

(32) Korolev, V. A.; Nefedov, O. M. Direct IR spectroscopic study of the cyclopentadienyl radical. *Russ. Chem. Bull.* **1993**, 42 (8), 1436–1437.

(33) Leicht, D.; Kaufmann, M.; Schwaab, G.; Havenith, M. Infrared spectroscopy of the helium solvated cyclopentadienyl radical in the CH stretch region. *J. Chem. Phys.* **2016**, *145* (7), 074304.

(34) Burcat, A.; Dvinyaninov, M. Detailed kinetics of cyclopentadiene decomposition studied in a shock tube. *Int. J. Chem. Kinet.* **1997**, 29 (7), 505–514.

(35) Kern, R. D.; Zhang, Q.; Yao, J.; Jursic, B. S.; Tranter, R. S.; Greybill, M. A.; Kiefer, J. H. Pyrolysis of cyclopentadiene: Rates for initial C–H bond fission and the decomposition of $c-C_5H_5$. Symp. (Int.) Combust, [Proc.] **1998**, 27 (1), 143–150.

(36) Roy, K.; Horn, C.; Frank, P.; Slutsky, V. G.; Just, T. Hightemperature investigations on the pyrolysis of cyclopentadiene. *Symp.* (*Int.*) *Combust,* [*Proc.*] **1998**, 27 (1), 329–336.

(37) Knyazev, V. D.; Slagle, I. R. Kinetics of the reaction between propargyl radical and acetylene. *J. Phys. Chem. A* **2002**, *106* (23), 5613–5617.

(38) Stahl, F.; Schleyer, P. v. R.; Schaefer Iii, H. F.; Kaiser, R. I. Reactions of ethynyl radicals as a source of C4 and C5 hydrocarbons in Titan's atmosphere. *Planet. Space Sci.* **2002**, *50* (7), 685–692.

(39) Savee, J. D.; Selby, T. M.; Welz, O.; Taatjes, C. A.; Osborn, D. L. Time- and isomer-resolved measurements of sequential addition of acetylene to the propargyl radical. *J. Phys. Chem. Lett.* **2015**, *6* (20), 4153–4158.

(40) Longuet-Higgins, H. C.; McEwen, K. L. Electronic spectra of cyclic aromatic hydrocarbon radicals and ions. *J. Chem. Phys.* **1957**, *26* (4), 719–723.

(41) Bouman, N. Calculations of the lower excited energy levels of the cyclic polyenes, radicals, and ions. J. Chem. Phys. **1961**, 35 (5), 1661–1664.

(42) Kuhn, J.; Čársky, P.; Zahradník, R. SCF-CI MO treatment of radicals having degenerate ground states. *Theor Chim Acta* **1974**, 33 (3), 263–268.

(43) Moskaleva, L. V.; Lin, M. C. Unimolecular isomerization/ decomposition of cyclopentadienyl and related bimolecular reverse process: ab initio MO/statistical theory study. *J. Comput. Chem.* **2000**, *21* (6), 415–425.

(44) Jamal, A.; Mebel, A. M. An ab initio/RRKM study of the reaction mechanism and product branching ratios of the reactions of ethynyl radical with allene and methylacetylene. *Phys. Chem. Chem. Phys.* **2010**, *12* (11), 2606–2618.

(45) da Silva, G. Mystery of 1-vinylpropargyl formation from acetylene addition to the propargyl radical: an open-and-shut case. J. Phys. Chem. A 2017, 121 (10), 2086–2095.

(46) Lee, Y. T.; McDonald, J. D.; LeBreton, P. R.; Herschbach, D. R. Molecular beam reactive scattering apparatus with electron bombardment detector. *Rev. Sci. Instrum.* **1969**, *40* (11), 1402–1408.

(47) Negru, B.; Goncher, S. J.; Brunsvold, A. L.; Just, G. M. P.; Park, D.; Neumark, D. M. Photodissociation dynamics of the phenyl radical via photofragment translational spectroscopy. *J. Chem. Phys.* **2010**, *133* (7), 074302.

(48) Negru, B.; Just, G. M. P.; Park, D.; Neumark, D. M. Photodissociation dynamics of the tert-butyl radical via photofragment translational spectroscopy at 248 nm. *Phys. Chem. Chem. Phys.* **2011**, 13 (18), 8180–8185.

(49) Kohn, D. W.; Clauberg, H.; Chen, P. Flash pyrolysis nozzle for generation of radicals in a supersonic jet expansion. *Rev. Sci. Instrum.* **1992**, 63 (8), 4003–4005.

(50) Friderichsen, A. V.; Shin, E.-J.; Evans, R. J.; Nimlos, M. R.; Dayton, D. C.; Ellison, G. B. The pyrolysis of anisole $(C_6H_5OCH_3)$ using a hyperthermal nozzle. *Fuel* **2001**, *80* (12), 1747–1755.

(51) Scheer, A. M.; Mukarakate, C.; Robichaud, D. J.; Ellison, G. B.; Nimlos, M. R. Radical chemistry in the thermal decomposition of anisole and deuterated anisoles: an investigation of aromatic growth. J. Phys. Chem. A 2010, 114 (34), 9043–9056.

(52) Harrison, A. G.; Honnen, L. R.; Dauben, H. J.; Lossing, F. P. Free radicals by mass spectrometry. XX. Ionization potentials of cyclopentadienyl and cycloheptatrienyl radicals. *J. Am. Chem. Soc.* **1960**, 82 (21), 5593–5598.

(53) Zhong, X.; Bozzelli, J. W. Analysis of anisole and phenoxy radical decomposition kinetics. *Chem. Phys. Processes Combust.* **1993**, 125–128.

(54) Daly, N. R. Scintillation type mass spectrometer ion detector. *Rev. Sci. Instrum.* **1960**, *31* (3), 264–267.

(55) Schissel, P.; McAdoo, D. J.; Hedaya, E.; McNeil, D. W. Flash vacuum pyrolysis. III. formation and ionization of cyclopentadienyl, cyclopentadienyl nickel, and dihydrofulvalene (dicyclopentadienyl) derived from nickelocene. *J. Chem. Phys.* **1968**, *49* (11), 5061–5066.

(56) Lossing, F. P.; Holmes, J. L. Stabilization energy and ion size in carbocations in the gas phase. J. Am. Chem. Soc. **1984**, 106 (23), 6917–6920.

(57) Hansen, N.; Klippenstein, S. J.; Miller, J. A.; Wang, J.; Cool, T. A.; Law, M. E.; Westmoreland, P. R.; Kasper, T.; Kohse-Höinghaus, K. Identification of C_5H_x isomers in fuel-rich flames by photoionization mass spectrometry and electronic structure calculations. *J. Phys. Chem.* A **2006**, *110* (13), 4376–4388.

(58) Beyer, T.; Swinehart, D. F. Algorithm 448: number of multiplyrestricted partitions. *Commun. ACM* **1973**, *16* (6), 379.

(59) Astholz, D. C.; Troe, J.; Wieters, W. Unimolecular processes in vibrationally highly excited cycloheptatrienes. I. Thermal isomerization in shock waves. *J. Chem. Phys.* **1979**, *70* (11), 5107–5116.

(60) Frank, P.; Herzler, J.; Just, T.; Wahl, C. High-temperature reactions of phenyl oxidation. *Symp. (Int.) Combust., [Proc.]* **1994**, *25*, 833–840.

(61) Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. Cyclopentadienylidene. A matrix-isolation study exploiting photolysis with unpolarized and plane-polarized light. *J. Am. Chem. Soc.* **1981**, 103 (17), 5190–5195.

(62) Cole-Filipiak, N. C.; Shapero, M.; Negru, B.; Neumark, D. M. Revisiting the photodissociation dynamics of the phenyl radical. *J. Chem. Phys.* **2014**, *141* (10), 104307.

(63) Herschbach, D. R. Reactive Scattering in Molecular Beams. In *Advances in Chemical Physics*; John Wiley & Sons, Inc.: 1966; pp 319–393.

(64) Harich, S. A. PHOTRAN, a program for forward convolution analysis of photodissociation, 2003.

(65) Fitch, W. L.; Sauter, A. D. Calculation of relative electron impact total ionization cross sections for organic molecules. *Anal. Chem.* **1983**, 55 (6), 832–835.

(66) NIST Mass Spec Data Center; Stein, S. E., director. Mass Spectra. In *NIST Chemistry WebBook, NIST Standard Reference Database Number* 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899.

(67) Robinson, J. C.; Sveum, N. E.; Goncher, S. J.; Neumark, D. M. Photofragment translational spectroscopy of allene, propyne, and propyne- d_3 at 193 nm. *Mol. Phys.* **2005**, *103* (13), 1765–1783.

(68) Ramphal, I. A.; Shapero, M.; Haibach-Morris, C.; Neumark, D. M. Photodissociation dynamics of fulvenallene and the fulvenallenyl radical at 248 and 193 nm. *Phys. Chem. Chem. Phys.* **2017**, *19* (43), 29305–29314.

(69) Lucas, M.; Song, Y.; Zhang, J.; Brazier, C.; Houston, P. L.; Bowman, J. M. Ultraviolet photodissociation dynamics of the 1propenyl radical. J. Phys. Chem. A 2016, 120 (27), 5248-5256.

(70) Pachner, K.; Steglich, M.; Hemberger, P.; Fischer, I. Photodissociation dynamics of the ortho- and para-xylyl radicals. *J. Chem. Phys.* **2017**, *147* (8), 084303.