Photoionization of the C₄H₅ Isomers

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ABSTRACT

Single-photon, photoelectron-photoion coincidence spectroscopy is used to record the mass-selected ion spectra and slow photoelectron spectra of C_4H_5 radicals produced by the abstraction of hydrogen atoms from three C_4H_6 precursors by fluorine atoms generated by a microwave discharge. Three different C_4H_5 isomers are identified, with the relative abundances depending on the nature of the precursor (1-butyne, 1,2-butadiene, and 1,3-butadiene). The results are compared with our previous work using 2-butyne as a precursor [Hrodmarsson, H. R. et al. *J. Phys. Chem. A* **2019**, *123*, 1521-1528]. The slow photoelectron spectra provide new information on the three radical isomers that is in good agreement with previous experimental and theoretical results [Lang, M. et al., *J. Phys. Chem. A* **2015**, *119*, 3995-4000; Hansen, N. et al., *J. Phys. Chem. A* **2006**, *110*, 3670-3678]. The energy scans of the C_4H_5 photoionization signal are recorded with substantially better resolution and signal-to-noise ratio than in earlier work, allowing the observation of autoionizing resonances based on excited states of the C_4H_5 cation. Photoelectron images recorded at several energies are also reported, providing insight into the decay processes of these excited states. Finally, in contrast to the earlier work using 2-butyne as a precursor, where H-atom abstraction was the only observed process, F-atom and H-atom addition to the present precursors are also observed through the detection of C_4H_6F , C_4H_5F , and C_4H_7 .

I. INTRODUCTION

Small hydrocarbon radicals play an important role in pyrolysis and combustion chemistry,^{1,2} atmospheric photochemistry,³ and interstellar chemistry.⁴ While considerable progress has been made in the study of the smallest such radicals, the complexity of the spectroscopy and chemistry grows rapidly with increasing size of the radical. In the present work, we focus on the C₄H₅ isomers⁵⁻¹³ produced by using a F-atom source to abstract H atoms from a series of C₄H₆ precursors, specifically 1-butyne (CH₃-CH₂-C≡CH), 1,2-butadiene (CH₃-CH=C=CH₂), and 1,3-butadiene (CH₂=CH-CH=CH₂). Our goal is to characterize the energetics and dynamics of these C₄H₅ radicals and their cations, and to understand how these characteristics depend on the nature of the isomers. This work complements our earlier work in which 2-butyne was used as a precursor for the CH₃CCCH₂ radical allowing the measurement of the slow photoelectron spectrum (SPES), the energy dependence of the C₄H₅ photoionization signal, and the absolute photoionization cross section of this isomer.⁵

Theoretical studies have allowed the identification of a number of different C₄H₅ species, of which six are not branched.⁶⁻¹⁰ These different 4-carbon isomers are given in Table I. The most recent theoretical values for the corresponding heats of formation^{8,10} are also given in Table II. As expected, the heats of formation of the resonance stabilized radicals (species (1) to (4) with two nominal structures and a delocalized unpaired electron, see Table I) are substantially lower than those of the non-resonance-stabilized CH₂CH₂CCH (5) and CH₂CHCHCH (n-C₄H₅) (6) isomers. Furthermore, while the heat of formation of the cyclic radical (4) is close to that of the other resonance stabilized radicals,⁸ entropy arguments indicate the population in the cyclic isomer may be small for the processes relevant here.

These considerations suggest that unless there are substantial rearrangements of the radical, hydrogen abstraction from each precursor will lead to a selected set of C₄H₅ isomers. For example, H-atom abstraction from 2-butyne is expected to produce CH₃CCCH₂ (1), and this is exactly what

was observed in our previous study.⁵ Although H-atom abstraction from 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$) can occur from two sites, only abstraction from a secondary C atom results in a resonance stabilized radical, $\text{CH}_2\text{CHCCH}_2$ (3), which is therefore expected as the dominant product. (The $\text{CH}_2\text{CHCCH}_2$ radical is also known as i- C_4H_5 .) Similarly, H-atom abstraction from 1-butyne ($\text{CH}_3\text{CH}_2\text{CCH}$) can occur from three sites, but only abstraction from the methylene group leads to a resonance stabilized radical, CH_3CHCCH (2). Finally, H-atom abstraction from 1,2-butadiene, $\text{CH}_3\text{CHCCH}_2$, can occur from 3 sites, and each process results in a different resonance stabilized radical: $\text{CH}_2\text{CHCCH}_2$ (3), CH_3CCCH_2 (1), and CH_3CHCCH (2). Since all three product radicals have similar $\Delta_f H^\circ$, the expectation is that significant quantities of all three radicals will be produced. The results of the present experiments are consistent with these expectations.

In what follows, we first use the ability to prepare selected radicals to record mass-selected slow photoelectron spectra (SPES)^{14,15} for CH_3CCCH_2 , CH_3CHCCH , and $\text{CH}_2\text{CHCCH}_2$ (species (1), (2) and (3) of Table I). Threshold photoelectron spectra (TPES) have been reported previously for the first two of these,¹⁶ but not for the third. The spectra provide information on the energetics and vibrational structure of C_4H_5^+ cation isomers. We then present the mass-selected photoionization spectra from the different precursors, and use these to identify resonant structure converging to excited states of the C_4H_5^+ ions. Mass-selected photoelectron spectra are then presented at selected photon energies, providing additional insight into the ionization processes. In our earlier work on CH_3CCCH_2 ,⁵ we also determined the absolute photoionization cross section of the radical by comparing the decrease in the precursor ion signal with the increase in the C_4H_5^+ signal. This approach is only possible if the H-atom abstraction from the precursor is the dominant reaction, or if the rate constants of all the competing reactions are known. Unfortunately, for the present precursors, F-atom addition occurs quite efficiently prior to H-atom loss, precluding the direct measurement of the radical photoionization cross section. (Indeed, the H-atom abstraction products that we observe may actually be produced by a reaction mechanism involving F addition to the precursor followed by HF elimination.) We can, however, obtain new information on the products

of F-addition. Furthermore, the H atoms produced following F-atom addition are found to react with precursor molecules, leading to the observation of C_4H_7 radicals under some conditions. We conclude the paper with a discussion of how these new data can be used to assess the relative concentrations of different C_4H_5 radicals in more complex environments.

II. EXPERIMENT

The experimental approach and apparatus have been described in detail previously,^{5,15,17-20} and are only briefly outlined here. The experiments were performed at the DESIRS beamline of the Synchrotron SOLEIL, using the DELICIOUS III double-imaging photoelectron-photoion coincidence spectrometer.¹⁷⁻¹⁹ A gas filter filled with Kr was used to suppress the harmonics from the undulator. For the present investigations, a flow-tube source was installed in which F atoms were produced by using a microwave discharge to dissociate F_2 .^{20,21} The F atoms interacted with the precursor gas diluted in helium downstream of the mixing point in the flow tube. All three precursors (1-butyne, 1,2-butadiene, and 1,3-butadiene, 98-99% purity) are gases at room temperature and purchased from ABCR GmbH & Co. or Air Liquide. To optimize the production of the species of interest, the concentrations of precursor and F atom could be separately controlled by using mass-flow controllers. In addition, the interaction time of the reactants could also be varied by using a movable injector. The reaction mixture exited the flow tube and was skimmed twice before entering the interaction region of the spectrometer. While there is no direct measurement of the rotational temperature of the resulting radicals and other species in the reaction mixture, comparisons with other measurements suggest that the sample is rotationally thermalized to near room temperature.

The coincidence spectra were recorded by monitoring the signal as the photon energy was scanned across the range of interest. The photon energy was calibrated, and the accuracy of the calibration assessed, by using the SPES signal for He produced by the residual third harmonic of the photon source,²² and by using the SPES signal and the known ionization thresholds for methyl²³ and

propargyl²⁴ radicals. This calibration for the wavelength scans is expected to be accurate to better than 5 meV for all three samples. This uncertainty of the photon energy applies to both the SPES and ion-yield measurements reported here.

All of the present photon energy scans were recorded with a DC extraction field of 88.7 V/cm. This field results in a shift of the observed ionization energies²⁵ in the SPES from the field-free values by 0.0071 eV (57 cm⁻¹), or approximately two steps in the spectra reported here. The SPES peaks for He, CH₃, and C₃H₃ that are used for calibration are also shifted by this amount, so that peak positions using the calibrated energy axis in the SPES already include this electric field shift. Because the effect of the electric field on the total ion yield curve is more complex (thresholds are shifted in the same manner but resonances may be shifted or split only slightly), we have removed the expected 7.1 meV field shift from the energy axis of both the SPES and ion yield plots in the figures presented here. Thus, energies read off the SPES must be corrected for the field shift to give the field-free thresholds reported in the present tables.

The photoelectron-photoion coincidence data contain all the information necessary to extract the wavelength scans at the masses of interest, as well as the threshold or slow photoelectron spectra (TPES or SPES, respectively) at each mass. In addition to mass filtering, a filter was also applied to select a region of interest in the ion image that corresponds to the signal from the "molecular beam". This filtering rejects the signal arising from background gas, and results in better sensitivity and signal-to-noise (S/N) in the detection of low-density species such as radicals.²⁰ As described previously,^{14,15} the SPES were obtained by integrating the photoelectron signal along lines of constant ionic state for a range of energies between 0 and a selected maximum energy, KE_{max} , which is chosen as a compromise between the S/N ratio and resolution. The value of KE_{max} is either 50 meV or 100 meV in the data presented here, which results in an effective electron-kinetic-energy resolution of 17 meV or 23 meV, respectively.¹⁵

The present studies are limited to photon energies below the ionization energy of the corresponding precursor molecules. The ionization energies of these precursors and relevant radicals are given in Table III.^{5,8,16,22,26-28} Because the dissociative ionization thresholds for the precursors are all somewhat higher than their ionization energies, the present choice of energy regions eliminates any possible contribution of the precursor dissociative ionization to the ionization signals from the neutral radicals.

The photon energy bandwidth from the monochromator was ~ 6 meV at 7 eV photon energy, and increases to ~ 10 meV at 10 eV. Typical high-resolution wavelength scans of the coincidence signal (both the mass-selected SPES and mass-selected ion yields) were performed with 3 meV steps, acquisition times of 100 to 150 sec/point, and total scan times of $\sim 12 - 15$ hours. The flow of the sample can fluctuate over such long acquisition times. To address this issue, fast scans with larger steps were recorded across the same energy range to obtain the correct overall shape of the spectrum. The relative intensities in the fast and long scans were then fit to provide a correction function for the latter scans. The spectra were also corrected for the variation in photon intensity by using a Si AXUV100 photodiode whose efficiency across the energy range of the spectrum is known.

Fixed-energy photoelectron spectra were recorded by selecting photon energies and averaging the coincidence images for considerably longer times (typically one hour). For these measurements, in which the monochromator was set to a particular energy, the photon energy setting is expected to be accurate to 10 meV. The mass-selected photoelectron images were reconstructed by using the pBASEX algorithm²⁹ to give both the photoelectron energy distribution and photoelectron-energy-dependent angular distributions at these energies. The uncertainty in the electron kinetic energies is dominated by the uncertainty in the imaging spectrometer calibration, and it is estimated to be approximately 5% of the electron kinetic energy (i.e., ± 50 meV at 1 eV kinetic energy). Without proper corrections for the spatial response of the detector, inhomogeneities might

introduce significant uncertainty into the photoelectron angular distribution parameters extracted from the experiments, and we defer discussion of the angular distributions to a later date.

The Gaussian package of electronic structure codes³⁰ was used for the present Franck-Condon simulations of the ionizing transitions, as well as for the geometry optimizations and harmonic frequency calculations required as input for those calculations. The calculations³⁰ were performed using density functional theory with M06-2X/AVTZ functionals, and the transition moments were assumed to be independent of the vibration coordinates.

III. RESULTS AND DISCUSSION

1. The Slow Photoelectron Spectra of C₄H₅

Figure 1a shows the previously recorded C₄H₅ SPES at mass 53 for the 2-butyne precursor,⁵ which preferentially produces the CH₃CCCH₂ (2-butyne-1-yl) isomer (1). Figure 1b shows the new C₄H₅ SPES recorded for the 1-butyne precursor, which preferentially produces the CH₃CHCCH (1-butyne-3-yl) isomer (2). Figure 1b is consistent with the threshold photoelectron spectrum for CH₃CHCCH previously reported by Lang *et al.*¹⁶ that was produced by using a pyrolysis source to generate the radical (lower panel of Figure 3 in Ref. 16). The lowest energy feature in Figure 1b appears at 7.959 eV, which is consistent with calculations for the X ¹A' state of the 1-butyne-3-yl cation.⁸ When corrected for the shift due to the DC electric field in the interaction region, this result yields an ionization energy of 7.966 ± 0.010 eV, where the error bar reflects the uncertainty in the photon energy and the rotational envelope of the ionizing transition. This value is consistent with the previously reported value of 7.97 ± 0.02 eV.¹⁶ This value is also slightly higher than the ionization energy of the CH₃CCCH₂ isomer (1) (7.93 ± 0.01 eV), as was noted previously.^{5,8,16} Table III summarizes the existing experimental and theoretical data on the ionization energies of C₄H₅ isomers, as well as the results of the present determinations.

Figure 1. (a) The previously reported⁵ SPES of C_4H_5 produced by using F atoms to abstract an H atom from 2-butyne. A Franck-Condon simulation for the first band in the SPES of CH_3CCCH_2 is also shown. (b) The SPES of C_4H_5 recorded in the same manner but using 1-butyne as the precursor. The effective resolution in both spectra is ~ 17 meV. A Franck-Condon simulation for the first band in the SPES of CH_3CHCCH is also shown.

Although the S/N ratio in Figure 1b is only moderate, some vibrational structure is still discernible. Figure 1b also shows a simulation of the spectrum obtained by using theoretical Franck-Condon factors convoluted with a linewidth of 30 meV to account for the spectral resolution and the

rotational contour of the bands, and scaling the result to the intensity of the origin band. The energy of the origin band in the present calculation is 7.92 eV, somewhat lower than the previous results of Hansen *et al.*⁸ of 7.95 eV, and the simulation in Figure 1b has been shifted slightly to match the observed threshold. Comparison of the experiment and theory allows the identification of three members of a progression in ν_{15}^+ , which corresponds to the single-bond CH₃-CH stretch, with a vibrational spacing of $\sim 800\text{ cm}^{-1}$. This progression of three bands was identified previously by Lang *et al.*¹⁶ The Franck-Condon simulation indicates there should be weak features associated with the ν_{20}^+ (199 cm^{-1}) and ν_{19}^+ (251 cm^{-1}) vibrations, but the S/N ratio makes it difficult to assign these definitively. [Note: for consistency, we use the numbering of the vibrational modes of Lang *et al.*,¹⁶ who numbered them from high to low frequency.]

Additional broad features are observed in Figure 1b between $\sim 8.6\text{ eV}$ and 8.9 eV , and at $\sim 9.57\text{ eV}$. Neither feature appears to be associated with the $X^+ \text{ } ^1A'$ ionic state, and the first triplet state of the 1-butyne-3-yl cation is predicted to lie at considerably higher energy (10.2 eV).⁸ These features may be associated with an excited singlet state of the cation, or to ionization of a different isomer. Although we do not have a candidate assignment for the weaker feature at 9.57 eV , one possible assignment for the $8.6 - 8.9\text{ eV}$ feature is the non-resonance-stabilized CH₂CH₂CCH radical (species (5)), which can be produced by H atom abstraction from the CH₃ group in 1-butyne. Although the theoretical adiabatic ionization energy for this isomer was previously reported to be 7.5 eV ,⁸ the present calculations indicate a much higher vertical ionization energy of $\sim 9\text{ eV}$. Thus, structure from this isomer between 8.6 and 8.9 eV in the SPES would not be surprising. Interestingly, the CH₂CH₂CCH isomer cannot be produced from 1,2-butadiene by simple abstraction of a single H atom. As seen below, no structure is observed in this region of the SPES produced with that precursor, providing support for the proposed CH₂CH₂CCH isomer (5) as the source of the structure between 8.6 and 8.9 eV in Figure 1.

Figure 2 shows the C_4H_5 SPES recorded for the 1,3-butadiene precursor, which is expected to produce the CH_2CHCCH_2 isomer (3). Neither the SPES nor TPES of this isomer (CH_2CHCCH_2) has been reported previously. Hansen *et al.*⁸ have reported an experimental photoionization yield curve with an onset for the $CH_2CHCCH_2^+ X^+ {}^1A'$ state at 7.60 ± 0.05 eV. They also reported a corresponding theoretical ionization energy of 7.55 eV. After correcting the energy of the first SPES band in Figure 2 for the electric field shift, the present measurement yields an ionization energy of 7.55 ± 0.01 eV.

Figure 2. The SPES of C_4H_5 produced by using F atoms to abstract an H atom from 1,3-butadiene precursor. Also shown is a Franck-Condon simulation for the first band in the SPES of CH_2CHCCH_2 .

Figure 2 also shows the theoretical SPES produced from the calculated Franck-Condon factors between the neutral and ionic ground states, using our present theoretical value for the ionization energy of 7.54 eV. The Franck-Condon simulation shows strong progressions in the ν_{21}^+ (219 cm^{-1} harmonic) mode and the ν_{18}^+ (569 cm^{-1} harmonic) mode, and a weak progression in the ν_6^+ (1972

cm⁻¹ harmonic) mode. The overall shape of the experimental SPES matches the predicted Franck-Condon envelope, but only the ν_{18}^+ fundamental is even partially resolved. This observation may reflect overlap due to the rotational structure of the vibrational bands, or perhaps the presence of multiple conformers of the radical (for example, cis- and trans- isomers of CH₂=CH- $\dot{C}$ =CH₂). Nevertheless, the overall shape of the SPES and location of the threshold confirm its assignment to the CH₂CHCCH₂ isomer. The sharp features observed within the band are suggestive of vibrational structure but, as discussed below, although the 7.6 eV band is also observed in the spectrum obtained using 1,2-butadiene as a precursor, these sharp features are not reproduced.

At higher energy, specifically between 8.6 and 8.9 eV, the CH₂CHCCH₂ SPES shows a second broad feature, somewhat similar to the higher energy feature observed in the 1-butyne-3-yl spectrum. As in that case, the first triplet state of CH₂CHCCH₂⁺ lies at considerably higher energy. (The A⁺ ³A' state lies at 10.29 eV in the calculations of Hansen *et al.*⁸) The CH₂CH₂CCH radical proposed to explain the structure in this region of the C₄H₅ spectrum from 1-butyne cannot be formed by simple H-atom abstraction from 1,3-butadiene, although rearrangement upon abstraction cannot be ruled out. Another possibility is that this feature is associated with an excited singlet state of CH₂CHCCH₂⁺.

Figure 3 shows the C₄H₅ SPES recorded for the 1,2-butadiene precursor. Unlike the other precursors, H abstraction for any of the three carbon atoms with CH bonds results in a resonance stabilized radical, with the expected production of the 2-butyne-1-yl, 1-butyne-3-yl, and CH₂CHCCH₂ isomers. The contributions to the SPES from the former two radicals are expected to be somewhat overlapped. Indeed, Figure 3 clearly shows a contribution from the CH₂CHCCH₂ radical (3), and the structure around 8 eV indicates the presence *a priori* of both the 2-butyne-1-yl and 1-butyne-3-yl radicals. Before discussing this in more detail, it is also noteworthy that the C₄H₅ SPES in Figure 3 does not show any significant structure between 8.6 and 8.9 eV. Because Figure

3 contains contributions from the 1-butyne-3-yl and $\text{CH}_2\text{CHCCH}_2$ radicals, the lack of structure in this region suggests that the broad features observed in Figures 1b and 2 have another source.

Figure 3. The SPES of C_4H_5 (red curve) produced by using F atoms to abstract an H atom from 1,2-butadiene precursor. This precursor produces all three linear resonance-stabilized radicals. Also shown is the reconstruction (black curve) of the C_4H_5 SPES using a linear combination of the individual normalized SPES from 1-butyne, 2-butyne, and 1,3-butadiene. Each of the former spectra results from a single resonance-stabilized C_4H_5 isomer, while the spectrum from 1,2-butadiene contains contributions from all three isomers. The C_4H_5 linear combination shown corresponds to $0.35 \times (1\text{-butyne}) + 0.40 \times (2\text{-butyne}) + 0.25 \times (1,3\text{-butadiene})$. See text for details.

In principle, it should be possible to reconstruct the mixed SPES from the 1,2-butadiene precursor from the individual C_4H_5 spectra of the other precursors. This procedure could be used to provide branching fractions for the competing abstraction reactions. To extract these branching ratios, however, we require quantitative relative intensities of the SPES for the individual isomers to put

the three component spectra on the same scale.³¹⁻³² Typically, the absolute photoionization cross sections of the radicals could be used for this task, and the absolute photoionization cross section of CH_3CCCH_2 was reported previously.⁵ Unfortunately, as mentioned above, the competing fluorine addition channels preclude the determination of absolute photoionization cross sections with our standard method.^{5,21,33} Theoretical absolute photoionization cross sections have been reported for all three radicals,³⁴ but these cross sections only include direct ionization, and not autoionization processes. Unfortunately, the modeling of TPES and SPES is particularly difficult because the intensities can be strongly dependent on autoionization processes.³⁵ Thus, we are limited to a determination of the signal branching fractions, that is, the branching ratio times the cross section. The signal branching ratios can be used to extract the true branching ratios when we are able to assess the contribution of autoionization to the SPES. To make this determination, we assume the SPES up to 8.5 eV have the same integrated cross sections. The energy region up to 8.5 eV includes the full first photoelectron band of each isomer, but no higher energy bands. We then use these normalized spectra to reconstruct the C_4H_5 SPES from 1,2-butadiene.

The integrated areas of the SPES spectrum of Figure 3 and the individual SPES spectra of the three C_4H_5 isomers were normalized to an integrated area of 1 in the region between 7.4 and 8.5 eV. The experimental spectrum of Figure 3 was then reconstructed as a weighted linear combination of the three individual isomer spectra. Because only the $\text{CH}_2\text{CHCCH}_2$ spectrum contributes to the 7.6 eV band, this component was fit first, followed by the fit of the other two spectra to the structure above 7.9 eV. Figure 3 shows this reconstruction with weights of 0.40 (2-butyne-1-yl), 0.25 ($\text{CH}_2\text{CHCCH}_2$), and 0.35 (1-butyne-3-yl). The fit of the summed spectrum to the most intense peak is quite good.

2. The Photoionization Yield Spectra for C_4H_5

Figure 4 shows the photoionization yields for the C_4H_5^+ mass for the radicals produced by hydrogen abstraction from 2-butyne, 1-butyne, and 1,3-butadiene. The C_4H_5 spectrum from 2-

butyne was reported previously,⁵ while the latter two are new to the present work. Photoionization yield curves of a variety of C_4H_5 radicals have been presented previously at considerably lower resolution.^{8,34,36} As indicated by the SPES in Figures 1 and 2, the spectra in Figures 4 a – c correspond to the CH_3CCCH_2 (1), CH_3CHCCH (2), and CH_2CHCCH_2 (3) radicals, respectively. The CH_2CHCCH_2 spectrum is terminated at 9.0 eV, just below the ionization energy of 1,3-

Figure 4. The total ion yield curves for $C_4H_5^+$ (mass 53) generated from three different precursors: (a) 2-butyne, (b) 1-butyne, and (c) 1,3-butadiene. The dashed lines in parts (b) and (c) indicate the positions at which fixed-photon-energy photoelectron spectra were recorded.

butadiene ($9.06946 \pm 0.0019\text{eV}$),²⁷ where the intense signal from the parent interferes with the radical spectrum.

The most striking aspect of Figure 4 is the change in resonant structure across the three spectra, illustrating the high sensitivity of SPES and ion yield curves for distinguishing different isomers. As discussed previously,⁵ the CH_3CCCH_2 (1) spectrum shows significant, fairly well-resolved features. In contrast, the CH_3CHCCH (2) spectrum shows some partially resolved features on a rising background, while the $\text{CH}_2\text{CHCCH}_2$ (3) spectrum shows broad rises and plateaus, with little evidence of resonant features. This behavior suggests that the ion states on which the resonances are based are also likely to be better resolved for CH_3CCCH_2 than for the other species.

The structure in the CH_3CCCH_2 (1) spectrum has been described in detail previously.⁵ The structure in the CH_3CHCCH (2) spectrum is quite irregular. The resonant features begin to appear at about 0.3 eV above the first ionization threshold, and thus the structure must result from Rydberg series converging to excited electronic states of CH_3CHCCH , rather than to excited vibrational levels of the $X^+ {}^1\text{A}'$ ground state. The observed resonance energies are given in Table S1 of the Supporting Information. In principle, one might expect to see Rydberg series of states converging to the excited states of the ion. These series would follow the Rydberg formula:

$$E_n = E_{\text{ie}} - \mathcal{R}/(n-\delta)^2, \quad (1)$$

where E_n is the energy of the Rydberg state, E_{ie} is the ionization energy, $\mathcal{R}$ is the mass-corrected Rydberg constant for C_4H_5 (13.60555 eV),³⁷ n is the integral principal quantum number, and δ is the quantum defect. The quantum defect is expected to remain nearly constant for members of an unperturbed Rydberg series. Unlike the case of CH_3CCCH_2 (1), however, no obvious series emerge in the CH_3CHCCH (2) spectrum. This observation suggests that, over the relatively small range of principal quantum numbers for which resolved features are observed, perturbations create irregularities in the spectrum that are not readily disentangled. This congestion is not due to the photon resolution, which increases from 6-10 meV across the scans. The first excited ${}^3\text{A}$ state of

$\text{CH}_3\text{CHCCH}^+$ has been calculated to lie at 10.2 eV,⁸ outside the energy range of the present scan. (The ionization energy of 1-butyne is 10.178 ± 0.005 eV.²⁶) It is likely that some of the observed structure is based on that ionic state. Singlet excited states of $\text{CH}_3\text{CHCCH}^+$ have not yet been calculated. Recall, however, the broad feature in the SPES between 8.6 and 8.9 eV. If this were associated with a singlet excited state of $\text{CH}_3\text{CHCCH}^+$, there are no obvious series of resonances associated with this ionization threshold. The second weak feature at 9.57 eV in the SPES provides a more promising possible convergence limit for some of the observed resonances. Theoretical calculations to assess and assign the excited singlet states of the ion would be helpful.

The C_4H_5^+ ion yield spectrum for $\text{CH}_2\text{CHCCH}_2$ (3) shows no obvious resonance structure (see Figure 4c). Nevertheless, the ion signal exhibits an increased rate of rise at 7.85 eV and again at 8.4 eV. The SPES of Figure 2 shows no corresponding features at these energies, so the rises cannot reflect the opening of new ionization channels. In addition, with the exception of the fluorinated species discussed below, mass spectra recorded under these conditions do not show species heavier than the precursor. Thus, dissociative ionization of heavier species is not the source of these rises. These rises must therefore reflect the presence of broad, unresolved resonance structure in the ionization spectrum that is based on excited electronic states of $\text{CH}_2\text{CHCCH}_2^+$, or to continuum shape resonances. The first triplet state ($^3\text{A}''$) is predicted to lie at 10.29 eV,⁸ outside the range of the present work, but the rise in Figure 4 may result from unresolved resonances converging to this limit. If the SPES features at 8.696 and 8.908 eV are associated with singlet excited states of $\text{CH}_2\text{CHCCH}_2^+$, some of this structure may also be based on those states. Indeed, a significant rise in the ionization signal does appear to be associated with the SPES peak at 8.908 eV. Calculations of the singlet excited states of $\text{CH}_2\text{CHCCH}_2^+$ are necessary to assess this possibility.

As discussed above, the lack of sharp resonances in the $\text{CH}_2\text{CHCCH}_2$ spectrum may simply be due to the Franck-Condon activity in low-frequency vibrational modes resulting in unresolved

structure that appears as broad features in the spectrum. A second possibility is that the resonances in $\text{CH}_2\text{CHCCH}_2$ are lifetime broadened by fast autoionization or competing decay mechanisms.^{38,39} For example, if the resonances in $\text{CH}_2\text{CHCCH}_2$ undergo radiationless transitions (either internal conversion or intersystem crossing), not only could the lifetime of the excited states be reduced, but the quantum yield for ionization would also be reduced, as the final states for these processes would likely have lower electronic energy and higher vibrational energy. In the absence of collisions, such states will ultimately most likely dissociate. To explain the present results, such

Figure 5. The total ion yield curve (red curve) for C_4H_5^+ (mass 53) generated from 1,2-butadiene. This precursor produces all three linear resonance-stabilized radicals. Reconstruction of the C_4H_5 total ion signal (black curve) at mass 53 obtained by using 1,2-butadiene as a precursor. A linear combination of the individual C_4H_5^+ ion yields from 1-butyne, 2-butyne, and 1,3-butadiene was used to reproduce the ion yield from 1,2-butadiene. Each of the former spectra results from a single resonance-stabilized C_4H_5 isomer, while the spectrum from 1,2-butadiene contains contributions from all three isomers. The C_4H_5 linear combination shown corresponds to $0.45 \times (1\text{-butyne}) + 0.15 \times (2\text{-butyne}) + 0.40 \times (1,3\text{-butadiene})$. See text for details. The dashed lines indicate the positions at which fixed-photon-energy photoelectron spectra were recorded.

competing processes would have to be more effective in $\text{CH}_2\text{CHCCH}_2$ (3) than in the other two radicals.

Figure 5 shows the C_4H_5^+ ion yield curve produced by using the 1,2-butadiene precursor. As discussed for the corresponding SPES, this C_4H_5^+ curve contains contributions from the three resonance-stabilized C_4H_5 radicals produced by the other three precursors. As expected, the spectrum shows structure somewhat intermediate from that of Figure 4. As for the SPES, it should be possible to reconstruct the spectrum in Figure 5 from the three component spectra. The signal branching fractions were determined first by normalizing the integrated cross sections between 7.4 and 9.0 eV for $\text{CH}_2\text{CHCCH}_2$, CH_3CHCCH , and CH_3CCCH_2 and, following the approach described for the SPES above, using them to fit the experimental spectrum obtained with the 1,2-butadiene precursor. Figure 5 shows the reconstruction of experimental spectrum by using 0.4 ($\text{CH}_2\text{CHCCH}_2$), 0.45 (CH_3CHCCH), and 0.15 (CH_3CCCH_2). The synthetic spectrum is in excellent agreement with the observed spectrum from 1,2-butadiene across the full energy region.

The signal branching fractions extracted from the ion yield spectrum are somewhat different from those determined from the SPES. This observation may in part be due to the somewhat different energy window of the fits. More likely, however, this observation is a result of the assumptions used in the fits that the integrated photoionization cross sections are all equal and that the integrated SPES are all equal. In particular, as discussed above, intensities in TPES and SPES can be significantly affected by autoionization processes that enhance the intensities of some bands.³⁵ If this effect occurs in one or more of the SPES spectra, it is unlikely the integrated SPES will have the same ratio of intensities as the integrated photoionization cross sections. In particular, the ion yield spectrum of the CH_3CCCH_2 radical from 2-butyne shows a sharp resonance right at threshold, which could lead to a strong enhancement of the corresponding SPES signal. Such an effect would lead to larger fractional character of this isomer in the SPES than in the ion yield spectrum. Because of this effect and the difficulty in measuring accurate relative SPES intensities

for different species, in the present instance, where the photoionization yield curves are reasonably well-structured leading to an enhanced isomeric sensitivity, the determination of isomeric branching ratios is most likely best done using the ion yield curves and the absolute (or relative) photoionization cross sections.

In principle, the recently reported theoretical absolute photoionization cross sections³⁴ for the three relevant C₄H₅ radicals could be used to extract branching fractions for H atom abstraction in the F + 1,2-butadiene reaction, providing kinetic information on hydrogen abstraction from the three different sites in 1,2-butadiene. However, the photoionization cross sections of Huang et al.³⁴ only include direct photoionization processes, and do not include resonant processes like autoionization, and it is clear from Figure 4a and b that autoionization contributes substantially to the cross sections for CH₃CCCH₂ and CH₃CHCCH. A second issue is that the theoretical cross section for CH₃CCCH₂ is a factor of ~8 – 10 times greater than the previously determined experimental cross section,⁵ and the inclusion of resonant photoionization is only expected to increase this difference. Nevertheless, the relative theoretical cross-sections of the three radicals might be expected to be more precise than absolute values and, if we use them, we can put the measurements of Figure 5 on an absolute scale. The resulting branching fractions for the H atom abstraction from F + 1,2-butadiene are 0.48, 0.04, and 0.48, for CH₃CHCCH, CH₃CCCH₂, and CH₂CHCCH₂, respectively. Based on the number of each type of H atom in 1,2-butadiene the statistical branching fractions would be 0.50, 0.17, and 0.33. An experimental determination of the absolute cross sections for the CH₃CHCCH and CH₂CHCCH₂ radicals, or additional theoretical calculations of these cross sections should resolve the discrepancy for CH₃CCCH₂, and pin down these branching fractions. In principle, the present experimental data could be turned around; that is, theoretical knowledge of the relative magnitudes of the true branching fractions could be used with the present signal branching ratios to determine the relative magnitudes of the absolute photoionization cross sections of the relevant three C₄H₅ isomers.

3. Fixed-Energy Photoelectron Spectra

Figure 6 shows three reconstructed photoelectron spectra of C_4H_5 from 1-butyne that were recorded at photon energies of 8.72 eV, 9.11 eV, and 10.00 eV. The first energy lies within a broad autoionizing resonance of CH_3CHCCH , while the second and third energies lie on plateaus with some weaker resonance character. As expected, each spectrum shows a strong feature at the energy of the ground state band in the corresponding SPES (Figure 1b), but with less resolved vibrational structure. The two higher energy spectra show a second feature between 8.6 and 8.9 eV, that is, at the energy of the weaker second band in the SPES. This feature is relatively weak compared to the first band in the 9.11 eV spectrum, but it is nearly the same intensity as the first band in the 10.00 eV spectrum. These two spectra confirm the observation of a second band in the SPES, which we have tentatively assigned to the $CH_2CH_2CCH^+$ cation ground state.

Figure 6. The fixed-photon-energy photoelectron spectra at 8.72 eV, 9.11 eV, and 10.0 eV for CH_3CHCCH generated from 1-butyne. The lowest energy corresponds to a strong, broad autoionizing resonance, and the two higher energies correspond to weak resonances on top of strong ionization continua. See Figure 4b for details. The spectra have been displaced vertically for clarity.

Figure 7. (a) The fixed-photon-energy photoelectron spectra at 8.33 eV and 8.72 eV for $\text{CH}_2\text{CHCCH}_2$ generated from 1,3-butadiene. The two energies are located on slowly rising portions of the corresponding ion-yield curve. The lowest energy corresponds to a strong, broad autoionizing resonance, and the two higher energies correspond to weak resonances on top of strong ionization continua. See Figure 4c for details. (b) The fixed-photon-energy photoelectron spectra at 8.33 eV and 8.72 eV for C_4H_5 generated from 1,2-butadiene. These spectra include contributions from the three resonance-stabilized isomers of C_4H_5 . The lowest energy corresponds to a resonance in both CH_3CCCH_2 and CH_3CHCCH and a flat part of the ion-yield curve for $\text{CH}_2\text{CHCCH}_2$. See Figure 5 for details. The spectra in both frames have been displaced vertically for clarity.

Figure 7a shows two photoelectron spectra of the C_4H_5 radical produced from the 1,3-butadiene precursor and using a photon energy of 8.33 eV and 8.72 eV. The ion yield curve for this isomer

is relatively featureless, and these two energies correspond to gradually rising parts of the curve. The two energies are only sufficient to observe the electronic ground state of the expected ion in the photoelectron spectra. The two spectra are quite similar, and the envelope of the observed photoelectron band closely follows that of the SPES, which suggests that the envelopes are governed by the Franck-Condon factors and that the SPES is not strongly affected by autoionization processes. Although there are some modulations in the band envelope, these modulations differ in the two spectra, and may simply reflect the S/N ratio in the images used to extract the spectra.

Figure 7b shows the photoelectron spectra of the C_4H_5 radicals produced from the 1,2-butadiene precursor and using photon energies of 8.33 eV and 8.72 eV. The first energy corresponds to a resonance in both the CH_3CCCH_2 and CH_3CHCCH radical spectra (see Figure 4), and to a plateau in the CH_2CHCCH_2 radical spectrum. As a result, it is not surprising that there is a strong enhancement of the overlapping $CH_3CCCH_2^+$ and CH_3CHCCH^+ photoelectron bands relative to the CH_2CHCCH_2 bands in the spectrum recorded at 8.33 eV. The second energy corresponds to broader features in the CH_3CCCH_2 and CH_3CHCCH ion yield spectra, and the top of a rising region in the CH_2CHCCH_2 ion yield spectrum. In this spectrum, the relative intensity of the CH_2CHCCH_2 band is enhanced, but it is still significantly smaller than the CH_3CCCH_2/CH_3CHCCH photoelectron band.

4. Additional Species Produced in the Flow Tube: C_4H_7 , C_4H_6F , and C_4H_5F

As discussed in the Introduction, a number of additional reactions occur in the flow tube beyond the single H-atom abstractions from the precursors. Sequential abstraction of H atoms results in C_4H_4 and C_4H_3 species. An effort has been made to minimize sequential reactions in the present study, but the C_4H_4 and C_4H_3 species will be discussed in a future publication. A number of addition reactions involving H and F are also observed, and these are now discussed.

Figure 8. The SPES (black) and total ion yield curve (purple) for C_4H_7 (mass 55) generated from 1,3-butadiene. The spectra can be assigned to the 1-methylallyl radical.

Figure 8 shows the SPES for mass 55 produced by using the 1,3-butadiene precursor. The mass 55 signal results from C_4H_7 produced by H-atom addition to the precursor. Addition to a terminal carbon on 1,3-butadiene results in a resonance-stabilized 1-methyl allyl radical, $CH_3CHCHCH_2$. Addition to an internal carbon results in a $\cdot CH_2CH_2CHCH_2$ radical that is not resonance stabilized, suggesting this product will be less favored. Lang *et al.*¹³ have previously recorded the mass-selected TPES of the 1-methyl allyl radical, and determined ionization energies of 7.48 and 7.59 eV for the E- and Z- isomers, respectively. Our signal for mass 55 is rather weak and noisy, but the overall shape and position of the band in the SPES agrees well with the earlier result. The mass-analyzed ion yield spectrum is also shown in Figure 8, and displays no sharp structure, with a generally smooth, slowly rising shape. The rise in cross section above 8.5 eV most likely comes

from unresolved transitions to states converging to excited states of the cation. Fixed-energy photoelectron spectra recorded at 8.33 eV and 8.72 eV show relatively smooth envelopes reproducing the band shape of the SPES in Figure 8.

The addition of F atoms to precursor molecules is also observed for 1,3-butadiene and 1,2-butadiene. Unfortunately, the signal for the latter reaction is quite weak, so we now focus on the former reaction. In particular, by analogy with the H-atom addition to 1,3-butadiene, F-atom addition can produce the resonance-stabilized 1-fluoromethylallyl ($\text{CH}_2\text{FCHCHCH}_2$) radical or the non-resonance-stabilized $\cdot\text{CH}_2\text{CHFCHCH}_2$ radical. Gu *et al.*⁴⁰ have studied the F + 1,3-butadiene reaction by using crossed molecular beams, and concluded that the F-addition/H-elimination reaction proceeded through a long-lived complex. Theoretical calculations by Song *et al.*⁹ indicated that both the $\text{CH}_2\text{FCHCHCH}_2$ and $\text{CH}_2\text{CHFCHCH}_2$ complexes lie below the reactant and product asymptotes, with the former lying ~ 50 kJ/mol lower than the latter. The examination of the reaction energetics and transition states was inconclusive about which complex was more important for the reaction.

Figure 9 shows the SPES and ion yield for mass 73 from just above the first ionization threshold at 7.4 eV to 9 eV. The SPES shows two bands of nearly equal intensity, while the ion signal exhibits a slow gradual rise with no resolved resonant features, again most likely due to unresolved transitions converging to excited states of the cation. The fixed-photon-energy photoelectron spectrum for mass 73 recorded at 8.72 eV has the same overall shape as the SPES, but at somewhat lower resolution. The fixed-energy spectrum, not shown here, can be used to confirm the first ionization threshold of the radical, where the SPES data were missing. The resulting ionization energy (corrected for the field-induced shift) of the first band is 7.35 ± 0.05 eV, and that of the second band is 8.07 ± 0.03 eV.

Figure 9. The SPES (black) and total ion yield curve (purple) for C_4H_6F (mass 73) generated from 1,3-butadiene. The two bands in the SPES most likely arise from $CH_2CHFCHCH_2$ and $CH_2FCHCHCH_2$, in order of increasing energy.

In principle, it is possible that these two bands could correspond to the E- and Z- isomers of the 1-fluoromethylallyl radical. However, the splittings in the ionization energies of the corresponding C_4H_7 methyl allyl species are quite small (~ 0.02 eV),¹⁶ suggesting a different explanation is required. A more likely explanation is that they correspond to the two complexes observed in the earlier theoretical study. The present calculations of the ionization energies of $CH_2FCHCHCH_2$ and $\cdot CH_2CHFCHCH_2$ give values of 7.89 eV and 7.32 eV, respectively. These values, and the splitting between them, are in reasonably good agreement with the two observed band positions. The observation that the non-resonance stabilized radical has approximately the same intensity as the resonance stabilized radical is somewhat surprising. One possibility is that there are actually

more resonance-stabilized radicals but the photoionization cross section of the non-resonance-stabilized radicals is larger, but that remains to be determined. The present results suggest that a more detailed examination of these reactions would be informative.

Finally, Figure 10 shows the SPES and ion yield spectrum at mass 72 (C_4H_5F), produced by using the 1-butyne precursor. The SPES shows a clear progression of bands, with the $v_n^+ = 1, 2$, and 3 members showing an increasing splitting or broadening with increasing v_n^+ , with an approximate vibrational spacing of 0.17 - 0.20 eV (1350 - 1600 cm^{-1}). The electric-field-corrected ionization energy determined from the first SPES band corresponds to 9.249 ± 0.010 eV. The mass-analyzed ion yield curve shows a step at this threshold, along with a smooth undulating rise to ~ 9.75 eV, where the cross section plateaus. The fixed-photon-energy photoelectron spectrum at 10 eV (on

Figure 10. The SPES (black) and total ion yield curve (purple) for C_4H_5F (mass 72) generated from 1-butyne. The spectra can be assigned to $CH_3CHCCHF$.

this plateau) reproduces the intensity distribution of the bands in the SPES, albeit with somewhat lower resolution. Unfortunately, the energy range of Figure 10 lies close to or above the ionization energies of the other two C₄H₆ precursors (see Table III), and the corresponding spectra were not recorded for those species.

The most straightforward reaction to produce C₄H₅F from the radical is through the CH₃CHCCH + F reaction. The two resonance structures for CH₃CHCCH should lead to two different C₄H₅F structures: CH₃- $\dot{\text{C}}\text{H}-\text{C}\equiv\text{CH} + \text{F} \rightarrow \text{CH}_3\text{-CHF-C}\equiv\text{CH}$ and CH₃CH=C- $\dot{\text{C}}\text{H} + \text{F} \rightarrow \text{CH}_3\text{CH=C=CHF}$. The present theoretical value for the ionization energy of the former product is 10.49 eV, well above the observed threshold, while the present theoretical value for the latter product is 9.35 eV, in good agreement with the observed threshold. The only other isomer with a predicted ionization energy close to this value has a fluoromethylene cyclopropane structure, for which the present calculations yield a theoretical ionization energy of 9.36 eV. Formation of this compound under the present conditions requires closure of the ring and rearrangement of H atoms. The simplicity of the chemistry leading to the CH₃CH=C=CHF structure thus suggests that it is the observed product. Note that F atom addition to the CH₃CH₂CCH precursor, specifically, F addition to the CH end of the molecule followed by H elimination from the methylene group, would also lead to the observed CH₃CH=C=CHF product, and may actually be the dominant mechanism responsible for the present observations.

IV. CONCLUSION

We have used photoelectron-photoion coincidence imaging techniques to record slow photoelectron spectra, mass-analyzed ion-yield spectra, and fixed-photon-energy photoelectron spectra of C₄H₅ radicals produced by H-atom abstraction from three different precursors: 1-butyne, 1,3-butadiene, and 1,2-butadiene. Combining these new data with our previous data on C₄H₅ radicals produced by H-atom abstraction from 2-butyne, we now have isolated SPES and ion-yield spectra for three resonance-stabilized radicals: CH₃CCCH₂, CH₃CHCCH, and CH₂CHCCH₂.

These data can be used to assess the contributions of each isomer to spectra resulting from a mixture of the three isomers. While this allows the determination of the signal branching fractions, the determination of the true branching fractions for each isomer requires the absolute photoionization cross sections of the three C_4H_5 radicals. The absolute photoionization cross sections for CH_3CHCCH and CH_2CHCCH_2 could not be determined with the present experimental approach, and the recently reported theoretical absolute photoionization cross sections³⁴ disagree substantially from our results for the CH_3CCCH_2 cross section.⁵ Further experimental and theoretical work to address this discrepancy is needed. The experimental determination of these radical cross sections will require the use of complementary techniques (see, for example, Refs. 41-46).

Beyond the work on C_4H_5 , the present work illustrates how F atom chemistry involving addition to both precursors and radicals, complex formation, and addition/elimination reactions can be important in some instances. The characterization of intermediates and branching among products would provide considerable insight into the relevant reaction mechanisms. Because abstraction reactions with F atoms are typically quite exothermic, these systems may also prove valuable in studies of non-thermal effects in reaction kinetics.

Supporting Information Available: The supporting information includes a table of the resonance positions in the CH_3CHCCH ion yield spectrum.

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Table I. Formulae and nominal structures of the C₄H₅ isomers displaying no branching. In the last column are given the precursor(s) used in the H-abstraction flow-tube source to yield the corresponding isomer in the present study.

Formula <i>Name</i>	Nominal structure	Main precursor (H-abstraction source)
(1) CH ₃ CCCH ₂ <i>2-butyne-1-yl</i>	(CH ₃ -C≡C- $\dot{\text{C}}\text{H}_2 \leftrightarrow \text{CH}_3\text{-}\dot{\text{C}}\text{=C=CH}_2$)	2-butyne; 1,2-butadiene
(2) CH ₃ CHCCH <i>1-butyne-3-yl</i>	(CH ₃ - $\dot{\text{C}}\text{H-C}\equiv\text{CH} \leftrightarrow \text{CH}_3\text{-CH=C=}\dot{\text{C}}\text{H}$)	1-butyne; 1,2-butadiene
(3) CH ₂ CHCCH ₂ <i>i-C₄H₅</i>	(CH ₂ =CH- $\dot{\text{C}}\text{=CH}_2 \leftrightarrow \dot{\text{C}}\text{H}_2\text{-CH=C=CH}_2$)	1,3-butadiene; 1,2-butadiene
(4) -CH ₂ CHCHCH- <i>n-C₄H₅</i>	(-CH ₂ - $\dot{\text{C}}\text{H-CH=CH-} \leftrightarrow \text{-CH}_2\text{-CH=CH-}\dot{\text{C}}\text{H-})$ cyclic	-
(5) CH ₂ CH ₂ CCH <i>1-butyne-4-yl</i>	($\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-C}\equiv\text{CH}$)	1-butyne
(6) CH ₂ CHCHCH <i>n-C₄H₅</i>	(CH ₂ =CH-CH= $\dot{\text{C}}\text{H}$, E and Z forms)	-

Table II. Heats of Formation of Selected C₄H₅ Radicals

	Radical	Resonance-Stabilized	$\Delta_f H^\circ$ (0 K) (kJ/mol)
(1)	CH ₃ CCCH ₂	Yes	318.5 ^a
(2)	CH ₃ CHCCH	Yes	329.3 ^a
(3)	CH ₂ CHCCH ₂	Yes	327.3 ^a
(4)	-CH ₂ CHCHCH-	Yes	342.1 ^a
(5)	CH ₂ CH ₂ CCH	No	389.1 ^b
(6)	CH ₂ CHCHCH	No	371.6 ^a

a. Reference 10. The quoted 2 σ uncertainty is ± 1.0 -1.5 kJ/mol.

b. Reference 8.

Table III. First Ionization Energies of Relevant Radical Precursors and Radicals.

Formula	Species	<i>I.E.</i> (/ eV)			
		Experiment		Theory	
		Previous	This work	Previous ^a	This work
C ₄ H ₆	1-Butyne	10.178±0.005 ^b	-	-	-
	2-Butyne	9.562±0.005 ^b	-	-	-
	1,2-Butadiene	9.23±0.02 ^c	-	-	-
	1,3-Butadiene	9.06946±0.00019 _d	-	-	-
C ₄ H ₅	CH ₃ CHCCH (2)	7.97±0.02 ^e	7.966±0.010	7.95	7.92
	CH ₃ CCCH ₂ (1)	7.94±0.02 ^e 7.93±0.01 ^f	-	7.94	7.93
	CH ₂ CHCCH ₂ (3)	7.60±0.05 ^a	7.550±0.010	7.55	7.54
	-CH ₂ CHCHCH-	-	-	7.25	-
	CH ₂ CH ₂ CCH	-	-	7.50	9.0 (vertical)
	E-CH ₂ CHCHCH	-	-	7.10	-
	Z-CH ₂ CHCHCH	-	-	7.08	-
C ₄ H ₇	E-CH ₃ CHCHCH ₂	7.48±0.01 ^e	-	-	-
	Z-CH ₃ CHCHCH ₂	7.59±0.01 ^e	-	-	-
C ₄ H ₅ F	CH ₃ CHFCH	-	-	-	10.49
	CH ₃ CHCCHF	-	9.249±0.010	-	9.35
C ₄ H ₆ F	CH ₂ CHFCHCH ₂	-	7.35±0.05	-	7.32
	CH ₂ FCHCHCH ₂	-	8.07±0.03	-	7.89

(a) Reference 8. (b) Reference 26. (c) Reference 28. (d) Reference 27. (e) Reference 16. (f)
Reference 5.

FIGURE CAPTIONS

Figure 1. (a) The previously reported⁵ SPES of C_4H_5 produced by using F atoms to abstract an H atom from 2-butyne. A Franck-Condon simulation for the first band in the SPES of CH_3CCCH_2 is also shown. (b) The SPES of C_4H_5 recorded in the same manner but using 1-butyne as the precursor. The effective resolution in both spectra is ~ 17 meV. A Franck-Condon simulation for the first band in the SPES of CH_3CHCCH is also shown.

Figure 2. The SPES of C_4H_5 produced by using F atoms to abstract an H atom from 1,3-butadiene precursor. Also shown is a Franck-Condon simulation for the first band in the SPES of CH_2CHCCH_2 .

Figure 3. The SPES of C_4H_5 (red curve) produced by using F atoms to abstract an H atom from 1,2-butadiene precursor. This precursor produces all three linear resonance-stabilized radicals. Also shown is the reconstruction (black curve) of the C_4H_5 SPES using a linear combination of the individual normalized SPES from 1-butyne, 2-butyne, and 1,3-butadiene. Each of the former spectra results from a single resonance-stabilized C_4H_5 isomer, while the spectrum from 1,2-butadiene contains contributions from all three isomers. The C_4H_5 linear combination shown corresponds to $0.35 \times (1\text{-butyne}) + 0.40 \times (2\text{-butyne}) + 0.25 \times (1,3\text{-butadiene})$. See text for details.

Figure 4. The total ion yield curves for $C_4H_5^+$ (mass 53) generated from three different precursors: (a) 2-butyne, (b) 1-butyne, and (c) 1,3-butadiene. The dashed lines in parts (b) and (c) indicate the positions at which fixed-photon-energy photoelectron spectra were recorded.

Figure 5. The total ion yield curve (red curve) for $C_4H_5^+$ (mass 53) generated from 1,2-butadiene. This precursor produces all three linear resonance-stabilized radicals. Reconstruction of the C_4H_5 total ion signal (black curve) at mass 53 obtained by using 1,2-butadiene as a precursor. A linear

combination of the individual $C_4H_5^+$ ion yields from 1-butyne, 2-butyne, and 1,3-butadiene was used to reproduce the ion yield from 1,2-butadiene. Each of the former spectra results from a single resonance-stabilized C_4H_5 isomer, while the spectrum from 1,2-butadiene contains contributions from all three isomers. The C_4H_5 linear combination shown corresponds to $0.45 \times (1\text{-butyne}) + 0.15 \times (2\text{-butyne}) + 0.40 \times (1,3\text{-butadiene})$. See text for details. The dashed lines indicate the positions at which fixed-photon-energy photoelectron spectra were recorded.

Figure 6. The fixed-photon-energy photoelectron spectra at 8.72 eV, 9.11 eV, and 10.0 eV for CH_3CHCCH generated from 1-butyne. The lowest energy corresponds to a strong, broad autoionizing resonance, and the two higher energies correspond to weak resonances on top of strong ionization continua. See Figure 4b for details. The spectra have been displaced vertically for clarity.

Figure 7. (a) The fixed-photon-energy photoelectron spectra at 8.33 eV and 8.72 eV for CH_2CHCCH_2 generated from 1,3-butadiene. The two energies are located on slowly rising portions of the corresponding ion-yield curve. The lowest energy corresponds to a strong, broad autoionizing resonance, and the two higher energies correspond to weak resonances on top of strong ionization continua. See Figure 4c for details. (b) The fixed-photon-energy photoelectron spectra at 8.33 eV and 8.72 eV for C_4H_5 generated from 1,2-butadiene. These spectra include contributions from the three resonance-stabilized isomers of C_4H_5 . The lowest energy corresponds to a resonance in both CH_3CCCH_2 and CH_3CHCCH and a flat part of the ion-yield curve for CH_2CHCCH_2 . See Figure 5 for details. The spectra in both frames have been displaced vertically for clarity.

Figure 8. The SPES (black) and total ion yield curve (purple) for C_4H_7 (mass 55) generated from 1,3-butadiene. The spectra can be assigned to the 1-methylallyl radical.

Figure 9. The SPES (black) and total ion yield curve (purple) for C_4H_6F (mass 73) generated from 1,3-butadiene. The two bands in the SPES most likely arise from $CH_2CHFCHCH_2$ and $CH_2FCHCHCH_2$, in order of increasing energy.

Figure 10. The SPES (black) and total ion yield curve (purple) for C_4H_5F (mass 72) generated from 1-butyne. The spectra can be assigned to $CH_3CHCCHF$.