Ultraviolet Photodissociation Dynamics of the 1-Propenyl Radical
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ABSTRACT: Ultraviolet (UV) photodissociation dynamics of jet-cooled 1-propenyl radical (CHCHCH3) were investigated at the photolysis wavelengths from 224 to 248 nm using high-n Rydberg atom time-of-flight (HRTOF) technique. The 1-propenyl radicals were produced from 193 nm photolysis of 1-chloropropene and 1-bromopropene precursors. The photofragment yield (PFY) spectra of the H atom product have a broad peak centered at 230 nm. The H + C3H4 product translational energy distribution’s peak near ~8 kcal/mol, and the fraction of average translational energy in the total available energy, ⟨fT⟩, is nearly a constant of ~0.12 from 224 to 248 nm. The H atom product has an isotropic angular distribution with the anisotropy parameter β ≈ 0. Quasiclassical trajectory calculations were also carried out using an ab initio ground-state potential energy surface for dissociation of 1-propenyl at the excitation energy of 124 kcal/mol (230 nm). The calculated branching ratios are 60% to the methyl + acetylene products, 16% to H + propyne, 4% to H + allene, and 1% to H + cyclopropene. The experimental and calculated P(E_T) distributions of the H + C3H4 products at 230 nm are in a qualitative agreement, suggesting that the H + propyne dissociation is the main H atom product channel. The calculated dissociation time scale on the ground electronic state is ~1 ps, shorter than but close to the time scale of ~10 ps for the overall UV photodissociation implied by the isotropic H atom product angular distribution. The UV photodissociation mechanism of 1-propenyl can be described as unimolecular decomposition of hot 1-propenyl radical on the ground electronic state following internal conversion from the electronically excited states of 1-propenyl. 

INTRODUCTION

C3H5 radicals have four isomers, allyl (CH2CHCH3), 1-propenyl (CHCHCH3), 2-propenyl (CH2CCH3), and cyclo-propyl (c-C3H5). Among the three linear isomers, allyl is a resonance-stabilized radical and the smallest π-conjugated system with an odd number of π-electrons, while 1-propenyl and 2-propenyl are β- and α-CH3-substituted vinyl radicals, respectively. The C3H5 radicals are important in hydrocarbon combustion.1−5 Direct H atom abstraction reactions of propene to form the linear C2H3 radicals compete with addition reactions of propene in combustion conditions and become more important at higher temperatures.5−7 The allyl radical is a precursor in the formation of aromatic hydrocarbons, polycyclic aromatic hydrocarbons,
and soot,\textsuperscript{2–4} while isomerization and unimolecular dissociation of the 1-propenyl and 2-propenyl radicals are involved in the allyl kinetics in combustion.\textsuperscript{5,6}

The electronic excited states and spectroscopy of the allyl radical have been extensively studied experimentally and theoretically,\textsuperscript{9–19} while the studies on the 1-propenyl and 2-propenyl radicals are limited.\textsuperscript{20} The first electronic absorption band of allyl at 370–410 nm was assigned to the \( \tilde{A}^2A_1 \) (valence \( \pi \) and \( \pi^* \) → \( \pi \)) transition. A strong ultraviolet (UV) electronic absorption band with diffuse structure was observed in the 210–250 nm region,\textsuperscript{10–15} due to Rydberg \( n \) excitations to four Rydberg electronic excited states, \( \tilde{B}^2A_1(3s) \) (band origin 249.7 nm), \( \tilde{C}^2B_2(3p_v) \) (240.63 nm), \( \tilde{D}^2A_1(3s) \) (236.8 nm), and \( \tilde{E}^2B_1(3p_v) \) (~230.9 nm) of allyl.\textsuperscript{14,16} The transition to the \( \tilde{E}^2B_1(3p_v) \) state contributes most of the oscillator strength in the UV electronic band of allyl.\textsuperscript{14,16} There have been no experimental studies on the electronic spectroscopy of the 1-propenyl and 2-propenyl radicals so far, while there was only one theoretical study using the equation-of-motion coupled cluster methods (EOM-CCSD).\textsuperscript{20} The electronic excited states of 1-propenyl and 2-propenyl radicals have higher oscillator strengths.\textsuperscript{20}

Among the four \( \text{C}_3\text{H}_5 \) isomers, the photodissociation of the allyl radical has been extensively investigated. Figure 1 shows the energetics and dissociation pathways of the \( \text{C}_3\text{H}_5 \) isomers based on the theoretical work of Chen et al.\textsuperscript{21} and Narendrapurapu et al.\textsuperscript{9} Three H-loss dissociation channels, allene (\( \text{CH}_3\text{CCH}_2 \)) + \( \text{H} \), propyne (\( \text{CH}_2\text{CCH}_2 \)) + \( \text{H} \), and propyne (\( \text{C}_3\text{H}_4 \)) + \( \text{H} \), and two \( \text{CH}_3 \) losses, \( \text{CH}_3 + \text{C}_2\text{H}_2 \) (acetylene) and \( \text{CH}_3 + \text{C}_2\text{H}_2 \) (vinylidene), are available. The photodissociation dynamics of allyl via the \( \tilde{A}^2B_1 \) state has been examined in the near-UV region of 420–380 nm,\textsuperscript{22,23} and via the \( \tilde{B}^2A_1, \tilde{C}^2B_2, \) and \( \tilde{E}^2B_1 \) states in the UV region of 249–216 nm.\textsuperscript{21,22,24–26} In the near-UV region, the H-loss product channels of allyl have a product translational energy distribution \( P(E_T) \) peaking near zero and an isotropic angular distribution. It was proposed that the \( \tilde{A}^2B_1 \) state of allyl decays into the ground state and the hot allyl radical dissociates to allene + \( \text{H} \) directly and to propyne + \( \text{H} \) via isomerization to the 1- and 2-propenyl radicals with the direct loss of the central \( \text{H} \) atom to form allene as the major product channel.\textsuperscript{22,25} In the UV region from 249 to 216 nm, both the \( \text{H} \) atom loss and \( \text{CH}_3 \)-loss channels were experimentally observed and confirmed by trajectory calculations\textsuperscript{21,22,24–27} with the H-loss channel being more important and a branching ratio of the \( \text{H} \) loss to the \( \text{CH}_3 \) loss of 95:5 at 248 nm.\textsuperscript{21,22,25} The UV photodissociation mechanism of allyl was hot radical dissociation on the ground electronic state following internal conversion from the UV excited electronic states.\textsuperscript{21,22,24,26} The product translational energy release of the H-loss product channel is modest with the \( P(E_T) \) distributions peaking near 8.5 kcal/mol and the fraction of the average translational energy in the total excess energy, \( \langle E_T \rangle \), being ~0.2 from 249 to 216 nm.\textsuperscript{26} The \( \text{H} \) atom product angular distribution is isotropic. \( \text{H} \) atoms are produced mainly from direct dissociation of allyl to allene + \( \text{H} \), while isomerization to 1-propenyl or 2-propenyl is required to produce propyne + \( \text{H} \), with an allene + \( \text{H} \) and propyne + \( \text{H} \) ratio of 6:1 indicated by the trajectory calculations for an excitation energy of 115 kcal/mol (equivalent to the 248 nm photoexcitation energy).\textsuperscript{21} The \( P(E_T) \) of the \( \text{CH}_3 + \text{C}_2\text{H}_2 \) channel peaked at 16 kcal/mol.\textsuperscript{22} The \( \text{CH}_3 \) elimination channel requires a 1,3 sigmatropic \( \text{H} \) shift to 1-propenyl or sequential 1,2 \( \text{H} \) shifts from allyl to 2-propenyl to 1-propenyl.\textsuperscript{21,25,26}

As the intermediate in the unimolecular dissociation pathways of allyl to the propyne + \( \text{H} \) and \( \text{CH}_3 \) elimination channels, 1-propenyl has the same dissociation channels as allyl (Figure 1).\textsuperscript{9,21} C–C bond fission to produce \( \text{C}_2\text{H}_2 + \text{CH}_3 \), C–H bond fission to produce propyne + \( \text{H} \), and isomerization to allyl or 2-propenyl

Figure 1. Potential energy diagram of the \( \text{C}_3\text{H}_5 \) system. All the energies are referenced to that of the most stable isomer, allyl radical (global minimum, GM). The 1-propenyl, 2-propenyl, and cyclo-propyl isomers are labeled as LM2 (local minimum 2), LM1, and LM3, respectively, as in ref 21. Three H-loss dissociation channels and two \( \text{CH}_3 \)-loss channels are shown. The energetics and pathways are based on the theoretical calculations in ref 8 and 21, with zero point energy corrections. The vertical excitation energies of the 1-propenyl electronic excited states are based on ref 20 and are relative to 1-propenyl (LM2) at 24.0 kcal/mol. The bracket next to the excited electronic states indicates the photolysis wavelengths from 224 to 248 nm (starting from 1-propenyl, LM2) in this study.
radicals followed by C–H bond fission to allene + H or to cyclopropene + H.

\[
\text{CHCHCH}_3 \rightarrow \text{C}_3\text{H}_2 + \text{CH}, \quad \Delta H_{\text{m,n},0} = 23.1 \text{ kcal/mol}
\]

→ propyne + H, \quad \Delta H_{\text{m,n},0} = 30.5 \text{ kcal/mol}

→ allene + H, \quad \Delta H_{\text{m,n},0} = 31.6 \text{ kcal/mol}

→ \text{c–C}_3\text{H}_4 + \text{H}, \quad \Delta H_{\text{m,n},0} = 53.9 \text{ kcal/mol}

There has been no photodissociation study on the 1-propenyl radical so far. Niedzielski et al. investigated dissociation and isomerization of 1- and 2-propenyl radicals chemically activated by hot H atom addition to allene and propyne in a gas cell. At an excitation energy of 23 kcal/mol above the H + allene or H + propyne products, 1-propenyl was found to mainly undergo C–C bond cleavage to yield CH$_3$ + acetylene and to a lesser extent isomerize to the allyl radical. Morton et al. studied the unimolecular dissociation of the hot 1-propenyl radical from the secondary dissociation of cis-1-bromopropene at 193 nm. They found that the dominant channel is methyl elimination and the H elimination channel competes with the methyl elimination at higher energies.

The current work investigates the UV photodissociation dynamics of jet-cooled 1-propenyl radical for the first time. In the UV photolysis wavelength region from 224 to 248 nm, the H atom photofragment yield (PFY) spectra (i.e., action spectra) of the 1-propenyl radical are obtained, identifying its UV absorption feature for the first time. The H atom time-of-flight (TOF) spectra using different precursors are recorded and transformed to the product translational energy distributions. The H atom product angular distributions are obtained. The unimolecular dissociation rate of the 1-propenyl is measured with the pump–probe delay in the UV region. Quasi-classical trajectory calculations are also carried out to compare the dynamic information from the experiment and to provide more insight into the dissociation dynamics of the 1-propenyl radical.

### EXPERIMENTAL AND COMPUTATIONAL METHOD

The HRTOF technique and experimental setup have been described in previous studies. The precursors used to generate the 1-propenyl radical were 1-chloropropene (98%, MP Biomedicals) and 1-bromopropene (95%, Acros Organics). 1-Bromopropene has been used as a precursor for the 1-propenyl radical in previous studies. A gas mixture of ~2% precursor seeded in Ar (at a total pressure of ~120 kPa) was expanded from a pulsed valve (General Valve, Series 9) through a 2 mm diameter nozzle; the precursor in expanded gas mixture was photolized right in front of the nozzle by 193 nm radiation from an ArF excimer laser, producing a pulsed 1-propenyl radical beam. The 1-propenyl radical beam was characterized using 121.6 nm vacuum ultraviolet (VUV) photoionization TOF mass spectrometry (TOFMS). The 1-propenyl radicals were photodissociated by a slightly focused UV photolysis laser radiation (at 220–250 nm, 0.2–1.3 mJ/pulse, line width 0.3 cm$^{-1}$). A Fresnel-Rhomb achromatic λ/2 plate was used to rotate the polarization of the photolysis radiation for the H atom product angular distribution measurements. The H atoms produced from the 1-propenyl photodissociation were tagged by two-color resonant excitation from 1S to 2P via the H atom Lyman-α transition at 121.57 nm and then further to a high-n Rydberg state by UV radiation at 366.24 nm. A small fraction of the metastable Rydberg H atoms drifted with their nascent velocities toward a microchannel plate (MCP) detector positioned perpendicular to the molecular beam and were field-ionized in front of the detector and detected. The nominal flight length was 37.02 cm, which was calibrated by 236 nm photodissociation of HBr with the well-known HBr dissociation energy and spin–orbit splitting energy of Br$(^2P_{3/2})$ and Br$(^2P_{1/2})$. The ion signals were amplified by a fast preamplifier, and the H atom TOF spectra were recorded and averaged using a multichannel scaler.

Quasiclassical trajectory calculations were carried out using the ab initio ground-state potential energy surface and method previously reported with the assumption that the electronically excited 1-propenyl radical undergoes internal conversion to the ground-state surface before the unimolecular dissociation. The trajectories were initiated with a starting geometry that corresponded to LM2, the 1-propenyl CH$_3$–CH–CH structure. Because the zero-point energy of LM2 is 14261.6 cm$^{-1}$, the total energy was chosen to be 57739.9 cm$^{-1}$ above LM2, which corresponded to a photon wavelength of 230 nm for excitation of the 1-propenyl radical from its lowest vibrational level. A total of 2200 trajectories were performed using steps of 0.125 fs, as previously described. The relative translational energy was determined from the final frame of each trajectory. The total reaction rate was determined as follows: a histogram, \( P(i) \), of the individual reaction times was constructed, giving the number of trajectories that reacted (to any product) in the time bin, \( i \), of about 0.65 ps width. The number of trajectories left unreacted at any time were counted as \( N(i) = N_{0} - \Sigma P(i) \). Finally, \( \ln[N(i)] \) was plotted as a function of time and determined the slope, which was equal to the reaction rate constant.

### RESULTS

The jet-cooled 1-propenyl radicals in the molecular beam from both the 1-chloropropene and 1-bromopropene precursor were characterized by VUV photoionization TOF mass spectrometry. The production of the C$_3$H$_5$ radicals from 193 nm photolysis of the precursors was identified at \( m/z \) 41 in the mass spectra. The nascent C–Br dissociation product translational energy release distribution of the 1-bromopropene precursor at 193 nm indicated that approximately 50% of 1-propenyl radicals produced were stable and the other 50% undergo dissociation or isomerization followed by dissociation. The stable 1-propenyl radicals were then cooled to low temperature in the supersonic expansion in the molecular beam. The resonance-enhanced multiphoton ionization (REMPI) spectrum of the allyl radical was searched for and the absence of any signal indicated that no allyl radicals were produced or stabilized from isomerization of the photolytically generated 1-propenyl radicals in the beam. The TOF spectra of the H atom products from the photodissociation of 1-propenyl were measured in the photolysis wavelength region of 224–248 nm with the photolysis laser polarization parallel and perpendicular to the flight path, respectively. Backgrounds have been properly removed, as described in previous studies. The TOF spectra using the 1-bromopropene precursor were also taken and they were similar to those from the 1-chloropropene precursor. The photolysis laser power was kept in the range of 0.2–1.3 mJ/pulse; the photolysis laser power dependence was measured, indicating little or no multiphoton dissociation contribution to the H atom product signals.

The H atom PFY spectra of 1-propenyl were obtained from integrating the net HRTOF spectra as a function of the UV
The net H atom TOF spectra of the jet-cooled 1-propenyl photodissociation are transformed to total center-of-mass (CM) $P(E_T)$ distribution. The CM translational energy of the products, $E_T$, is converted from the H atom flight time $t_H$ using the following equation

$$E_T = \left( 1 + \frac{m_H}{m_{C_3H_4}} \right) E_H = \frac{1}{2} \frac{m_H}{m_{C_3H_4}} \left( \frac{L}{t_H} \right)^2$$

where $E_H$ is the laboratory translational energies of the H atom photofragment and $L$ is the flight length. The resultant $P(E_T)$ distributions from the photodissociation of 1-propenyl at 226, 230, 232, and 240 nm using the 1-chloropropene precursor are shown in Figure 4 as examples. The $P(E_T)$ distributions have a broad feature that peaks at low translational energy ~8 kcal/mol and extends to the high energy of ~75 kcal/mol. The maximum available energy for the propyne + H, allene + H, and c-C$_2$H$_4$ + H channels are indicated in Figure 4. The translational energy release of the H atom loss dissociation channel of 1-propenyl is modest; for example, the average product CM translational energy $\langle E_T \rangle$ is 13.4 kcal/mol at 230 nm and 12.9 kcal/mol at 232 nm, and the fraction of $\langle E_T \rangle$ in the total available energy is $\langle f_T \rangle \approx 0.14$ for both wavelengths, assuming for the lowest energy product channel propyne + H. The $P(E_T)$ distributions at other photolysis wavelengths from 224 to 248 nm are similar to those at 230 and 232 nm, and the $\langle f_T \rangle$ values are in the range of 0.13–0.15 with an average of 0.12 and nearly a constant value from 224 to 248 nm (Figure 5). The $\langle f_T \rangle$ values using the 1-bromopropene precursor are also obtained at the photolysis wavelengths 224–248 nm and they are similar to but slightly smaller than those from the 1-chloropropene precursor, with an average of 0.11 from 225 to 248 nm (Figure 5).

The H atom product angular distributions in the UV photodissociation of 1-propenyl were examined using linearly polarized laser radiation. Figure 6 shows the H atom TOF spectra from the 1-propenyl photodissociation by linearly polarized 230 nm laser radiation. The polarization direction of the photolysis laser was set for clarity. The error bars indicate the maximum translational energies of the three H atom production channels. The energies are based on the theoretical dissociation energies of the three channels in refs 8 and 21.

**Figure 2.** H atom TOF spectra in the photodissociation of jet-cooled 1-propenyl radical at photolysis wavelengths 226, 230, 232, and 240 nm, respectively. The 1-propenyl radical was produced from 193 nm photolysis of 1-chloropropene precursor. The TOF spectra were net H atom TOF with the 193 nm photolysis radiation on minus off. The photolysis radiation polarization was parallel to the TOF axis (the H atom product angular distribution was shown to be isotropic). Each TOF spectrum was scaled to its maximum intensity.

**Figure 3.** H atom product yield (PFY) spectra of 1-propenyl as a function of photolysis excitation energy in the region of 224–248 nm. Open circles (○) represent the integrated HRTOF signals of 1-propenyl using the 1-chloropropene precursor, while the filled circles (●) represent those from the 1-bromopropene precursor. The signals were normalized to the same photolysis laser power and scaled to the maximum intensity. The spectra are offset for clarity. The error bars indicate the 95% confidence limit from multiple measurements.

**Figure 4.** CM $P(E_T)$ distributions of the 1-propenyl radical at 226, 230, 232, and 240 nm, respectively. Each distribution was normalized to its maximum. The vertical lines indicate the maximum translational energies of the three H atom production channels. The energies are based on the theoretical dissociation energies of the three channels in refs 8 and 21.
relative to the TOF axis is indicated in the figure. The H atom TOF spectra are basically identical, showing an isotropic angular distribution. The linearly polarized light preferentially excites the 1-propenyl radicals with their electronic transition dipole moment parallel to the electric E of the polarized light. The photofragment angular distribution is given by

$$I(\theta) = \frac{1}{4\pi}[1 + \beta P_2(\cos \theta)],$$

where $\beta$ is the anisotropy parameter ($-1 \leq \beta \leq 2$), $\theta$ is the angle between the electric vector of the polarized laser radiation E and the recoiling velocity vector of the H atom product (the direction of detection of the TOF axis), and $P_2(\cos \theta)$ is the second Legendre polynomial. Using this equation and the H atom TOF spectra at 230 nm, an anisotropy parameter $\beta \approx 0$ is derived (Figure 6).

The H atom product yield time profile in the UV photolysis of 1-propenyl was investigated by varying the delay time between the photolysis laser and probe laser. The time profile was obtained by integrating the HRTOF spectra as a function of the photolysis-probe delay time. The time profile can be used to obtain the microcanonical rate of the unimolecular dissociation of 1-propenyl. The initial rise is determined by the rate of H atom formation from 1-propenyl, while the decay of signal is because of the H atom flight out of the interaction region between the two beams. Figure 7 shows the time profiles of 1-propenyl from the 1-chloropropene precursor at 230 nm photolysis radiation and from the 1-bromopropene precursor at 236 nm. The time profiles of the H atom signals, $S_H(t)$, are fitted using an expression based on the previous work from Chen’s group to estimate the unimolecular dissociation rates of the 1-propenyl radical$^{35}$

$$S_H(t) = N[1 - \exp(-k_{1P}t)] \left[ \frac{1}{\exp\left(\frac{t-a}{b}\right) + 1} \right]$$

(2)

where $k_{1P}(t)$ is the unimolecular dissociation rate constant for the H atom formation from 1-propenyl, and $a$ and $b$ are constants that describe the width of the plateau region and the decay
The trajectory calculations for 1-propenyl photodissociation at 230 nm. The calculated distributions from the three H atom production channels are shown along with the total distribution.

The angular distribution of the H atom product from the H + propyne and H + allene product channels, respectively. The 5 atoms of the 1-propenyl radical are labeled in the figure. The geometry of the 1-propenyl radical (LM2) is from ref 21.

**DISCUSSION**

The UV photodissociation of the 1-propenyl radical in the wavelength range of 224–248 nm was investigated experimentally for the first time. The H atom products from the H + C3H4 dissociation channels were observed directly from the H atom TOF spectra. The H atom PFY spectra recorded using two different precursors of 1-propenyl are similar and reveal a broad UV absorption feature peaking at 230 nm, while no previously reported UV absorption spectrum of 1-propenyl is available for comparison. Kozioł et al. calculated the electronic excited states of 1-propenyl as a CH3-substituted vinyl. Two excited states, B2A″ (π* ← n, vertical excitation energy at 242 nm) and C2A′ (π* ← π, 221 nm), have their vertical electronic excitation energies in the studied region of 224–248 nm and are also predicted to have higher oscillator strengths. The observed UV absorption feature could then be due to either or both of these electronic excited states. Note that the H atom PFY spectrum represents only part of the UV absorption spectrum of 1-propenyl, as other product channels such as CH3 loss can be significant. As discussed next, the electronically excited 1-propenyl radical likely decays via internal conversion to the ground electronic state and then undergoes unimolecular dissociation on the ground-state surface. Our trajectory and RRKM calculations for the ground-state dissociation of 1-propenyl show that the CH3 loss is the dominant dissociation channel and H + propyne is the main H-loss product channel.

The angular distribution of the H atom product from the UV photodissociation of the 1-propenyl radical is isotropic (Figure 6). The isotropic distribution indicates that the time scale of the overall UV photodissociation of 1-propenyl is longer than the rotational period of the 1-propenyl radical. The rotational temperature of the 1-propenyl radical in the molecular beam is expected to around 15 K based on the previous study on the allyl radical. Assuming this temperature, the average rotational period of the 1-propenyl radical is estimated to be in the range of 10 ps. The pump−probe experiments in this study were limited by the 10 ns pulsed laser temporal resolution and can only show that the lower limit of the dissociation rate of the 1-propenyl radical at excitation wavelengths 230 and 236 nm is on the order of 108 s−1 (Figure 7). The angular distribution and pump−probe delay experiments suggest that the UV photodissociation time scale of the 1-propenyl radical is longer than 10 ps.
The trajectory calculations determined that the total reaction rate of 1-propenyl dissociation on the ground-state surface at the equivalent excitation energy of 230 nm was $1.3 \times 10^{12}$ s$^{-1}$ or a lifetime of 0.8 ps, close to the range of the time scale implied by the isotropic product angular distribution. Note that this calculated rate or lifetime is only for the unimolecular dissociation of 1-propenyl once it has reached the ground-state electronic surface after internal conversion and does not include the time for decay from the excited electronic states to the ground electronic state. In earlier studies on the electronically excited states of the allyl radical using picosecond time-resolved pump–probe photoelectron spectroscopy, the decay time of the $\tilde{B}A_1$ and $\tilde{C}B_1$ excited states of allyl in the 250–238 nm region were shown to range from 20 to 9 ps. $^{36,39}$ It is plausible that the excited states of 1-propenyl in the UV region have similar decay times. The overall UV photodissociation time scale of $>10$ ps implied by the isotropic angular distribution could then be consistent with the combined time scale of the decay of the electronic excited states ($>10$ ps) and the unimolecular dissociation on the ground electronic state ($\sim 1$ ps). Another uncertainty in the current experiment is that the degree of rotational excitation of the 1-propenyl radical was not actually measured and was not well established. If present in the 1-propenyl radical, high rotational excitation might both decrease the rate of dissociation and decrease the anisotropy, as observed in earlier investigations. $^{36,40–44}$

The CM $P(E_f)$ distributions for the H + C$_3$H$_4$ channel show small product translational energy release. The $P(E_f)$ distributions have the shape of a typical statistical distribution in unimolecular dissociation, peaking at a low energy of $\sim 8$ kcal/mol and extending to high kinetic energy, approaching the maximum available energy for the cyclopropene + H channel in a one-photon dissociation process of 1-propenyl. The onsets of the other two H-elimination channels, propyne + H and allene + H, are at higher energies ($\text{Figure 4}$). The experimental $P(E_f)$ distributions at various excitation wavelengths have similar shape and do not change significantly with increasing excitation energy (with only a small amount of increase in the translational energy release). The $\langle f_f \rangle$ values stay around 0.12 for the photolysis wavelength region of 224–248 nm ($\text{Figure 5}$). The observed $P(E_f)$ distributions support the dissociation mechanism of unimolecular decomposition of the hot 1-propenyl radical on the ground electronic state following internal conversion of the excited state.

The experimental $P(E_f)$ distribution alone cannot differentiate the contributions from the three H-loss dissociation channels. As shown in $\text{Figure 1}$, in addition to direct dissociation of 1-propenyl to CH$_3$ + C$_2$H$_2$ and H + propyne isomerization of 1-propenyl to 2-propenyl and allyl could compete and lead to the H + allene products. The trajectory calculations can help identify the branching ratios of the H-loss channels. Our trajectory calculations, along with the RRKM calculations, show that the H + propyne channel is the dominant H-loss channel, indicating that isomerization of 1-propenyl is not important and could not compete with the direct H-loss dissociation. This is consistent with the higher isomerization barrier than the direct H-loss barrier of 1-propenyl ($\text{Figure 1}$). The $P(E_f)$ distribution from the trajectory calculations for the H atom dissociation of 1-propenyl at the equivalent excitation of 230 nm is in qualitative agreement with the experimental $P(E_f)$ distribution at 230 nm ($\text{Figure 8}$). The overall H atom $P(E_f)$ distribution by the trajectories shows a peak around 10 kcal/mol, along with another peak near 20 kcal/mol, and extends to high kinetic energy of $\sim 60$ kcal/mol. The calculated $P(E_f)$ distribution has higher kinetic energy release and is more repulsive than the experimental one. The trajectory calculations also provide the $P(E_f)$ distributions for individual H-loss channels, which show that the H + propyne channel is dominant, the H + allene channel is significant, but the H + cyclopropene channel is of minor importance. This result is consistent with the reaction barrier for these three H-loss channels ($\text{Figure 1}$) with the c-C$_4$H$_5$ + H channel being the highest energy channel and requiring isomerization to allyl and then ring closing to form cyclo-propyl (c-C$_4$H$_2$). The dominant H + propyne channel has an exit barrier of 5.4 kcal/mol from 1-propenyl, and the peak of $\sim 8$ kcal/mol in the experimental $P(E_f)$ distribution is consistent with this barrier. The calculated $P(E_f)$ distribution peaks at higher energies, indicating that the calculated ground-state potential energy surface for the H + propyne dissociation channel might be more repulsive than the actual surface. It is unclear why there are two peaks in the calculated $P(E_f)$ distribution; better statistics in the trajectory calculations might smooth out the $P(E_f)$ distribution.

The trajectory calculations also identify the sites of the H atom loss and provide more insights into the dissociation dynamics ($\text{Figure 9}$). In the dominant H + propyne channel, removal of the vinylic H (H1) on the central C1 atom is the main pathway, mostly due to direct C–H bond fission in 1-propenyl ($\text{Figure 1}$). The number of trajectories of loss of H2 on the terminal C2 atom is about one-fifth of that of H1; this suggests that 1-propenyl undergoes 1,2 H shift to 2-propenyl which then loses either H1 or H2 to form propyne. The large H1 to H2 ratio indicates that direct C–H bond fission in 1-propenyl (over the 35.9 kcal/mol energy barrier) is more important than H-elimination from 2-propenyl after isomerization of 1-propenyl (over the 40.5 kcal/mol barrier) ($\text{Figure 1}$). In the minor H + allene channel, the removal of the central vinylic H1 is still more probable than that of the other four H atoms. The loss of H1 to form allene requires 1,3 sigmatropic H shift of one of the methyl H atoms (H3, H4, or H5) from 1-propenyl to allyl (over the 40.2 kcal/mol barrier) and then loss of the central H1 atom. The loss of H3, H4, and H5 suggest 1,2 H shift from 1-propenyl to 2-propenyl followed by loss of the methyl H atoms and/or sequential 1,2 H shifts to allyl and then H loss on the central C atom to H + allene. The loss of H2 is probably due to H1 and H2 scrambling in the 1,2 H shift isomerization between 1-propenyl and 2-propenyl and H2 and H3, H4, H5 scrambling in the 1,3 sigmatropic H shift isomerization between 1-propenyl and allyl, followed by the above dissociation mechanisms to H + allene. Note that direct methyl elimination from 1-propenyl is the lowest energy channel and has the lowest energy barrier among all the pathways of 1-propenyl. Indeed, the trajectory calculations show that this channel is more important than all the H atom channels. However, our current instrument and study could only provide measurements of the H-loss product channels.

Overall, the UV photodissociation of 1-propenyl radical is similar to that of the allyl isomer. Although the initial electronic excitation of allyl involves the 3s and 3p Rydberg states and that of 1-propenyl with most likely the valence $\pi^*$ state, both allyl and 1-propenyl undergo internal conversion and proceed to unimolecular dissociation on the ground electronic state. Consequently, the energetics and isomerization pathways determine the outcomes of the overall photodissociation. Although the H atom product $P(E_f)$ distribution and angular distribution of the allyl radical and the 1-propenyl radical are similar, there are significant differences in their unimolecular dissociation dynamics. The allyl radical, as the most stable C$_3$H$_5$ isomer, dissociates...
mainly to H + allene in a simple C−H bond rupture and to a lesser extent to H + propyne after isomerization to 1-propenyl and 2-propenyl over higher barriers; the CH3 loss channel is a minor channel as it also requires isomerization to 1-propenyl.

The 1-propenyl radical, 24.0 kcal/mol higher in energy than allyl, can dissociate to H + propyne in a simple C−H bond rupture and to a lesser extent to H + allene after isomerization to 2-propenyl and allyl; furthermore, 1-propenyl can directly dissociate to CH3 + C2H2 with the lowest energy barrier, making the CH3 elimination as indicated by the trajectory calculations) the main dissociation channel of 1-propenyl. Because of its lowest energy and higher dissociation and isomerization barriers, the allyl radical in the ground electronic state has a lifetime of 16 ps at 115 kcal/mol internal excitation energy (by trajectory calculations).21 1-Propenyl, due to its higher energy and lower dissociation barriers, dissociates faster in the ground electronic state and has a lifetime of ~1 ps at the excitation energy of 124 kcal/mol (230 nm).

■ CONCLUSION

The H atom product channel in the UV photodissociation of jet-cooled 1-propenyl radicals is studied at the photolysis wavelengths from 224 to 248 nm using the HRTOF technique. In this region, the H atom PFY spectra have a broad feature peaking at 230 nm and show the UV absorption feature of 1-propenyl for the first time. The H + C2H2 P(Ef) distributions peak near ~8 kcal/mol, and the fraction of average translational energy in the total excess energy, ⟨f⟩, is nearly a constant of ∼0.12 from 224 to 248 nm. The H atom product has an isotropic angular distribution. Quasi-classical trajectory calculations were also carried out for the excitation energy of 230 nm. The calculations give the products branching ratios of 60% to methyl + acetylene, 16% to H + propyne, 4% to H + allene, and 1% to H + cyclopropene, indicating that H + propyne dissociation is the predominant H atom product channel and isomerization of 1-propenyl to 2-propenyl and allyl is not significant. The calculated P(Ef) distribution of the H + C2H2 products at 230 nm is in a qualitative agreement with the experimental distribution but has a larger kinetic energy release, suggesting that the region of the H-loss channels on the calculated potential energy surface is somewhat too repulsive. The calculated dissociation time scale is ~1 ps, shorter than but close to the time scale of ~10 ps for the overall UV photodissociation implied by the isotropic H atom product angular distribution. The UV photodissociation mechanism of 1-propenyl is consistent with internal conversion from the electronically excited state of 1-propenyl followed by unimolecular decomposition of the hot radical on the ground electronic state.

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Notes
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