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Citation: *The Journal of Chemical Physics* **109**, 5372 (1998); doi: 10.1063/1.477156

View online: <http://dx.doi.org/10.1063/1.477156>

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UV photodissociation dynamics of allyl radical by photofragment translational spectroscopy

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(Received 26 February 1998; accepted 26 June 1998)

Photodissociation of the allyl radical, CH_2CHCH_2 , has been studied using the method of molecular beam photofragment translational spectroscopy following excitation to the $\tilde{\text{C}}(2^2B_1)$ and $\tilde{\text{A}}(1^2B_1)$ states by 248 and 351 nm photons. Two different primary channels have been detected following 248 nm excitation: H-atom loss (84%) and CH_3 elimination (16%). From the product translational energy distribution and polarization dependence studies, dissociation processes from the ground-state C_3H_5 potential energy surface are inferred for both wavelengths. At 248 nm there may also be a contribution to the H-atom loss channel from predissociation by a higher electronically excited state. Rice–Ramsperger–Kassel–Marcus (RRKM) calculations show that the formation of cyclopropene is not important, while formation of allene and methylacetylene from dissociation of 1- and 2-propenyl radicals are important reaction pathways at both wavelengths. Translational energy distributions peaking well away from zero provide evidence for CH_3 elimination directly from an allylic structure through a four-member cyclic transition state. © 1998 American Institute of Physics. [S0021-9606(98)02137-0]

I. INTRODUCTION

It is well known that neutral free radicals are important intermediate species in many important chemical processes. However, very often only limited information is available on these “transient” species (as compared to stable molecules), mainly owing to the difficulties in producing them under well defined conditions suitable for definitive experimental studies.

The allyl radical is the simplest conjugated π -electron hydrocarbon radical and represents a benchmark molecule for both theoretical and experimental studies. It is an intermediate in many thermal,¹ combustion,² photochemical,³ and surface catalytic^{4,5} reactions. The allyl radical has been the subject of many experimental and theoretical investigations. Electron-spin resonance (ESR)^{6,7} and electron diffraction⁸ showed that this radical has a planar structure with C_{2v} symmetry in its ground state. Photoelectron spectroscopy⁹ has been used to determine the vertical and adiabatic ionization potentials. Vibrational frequencies and structural information for the ground electronic state have been obtained from matrix infrared (IR),^{10,11} ultraviolet (UV) resonant Raman spectroscopy,^{12–16} and IR diode laser spectroscopy.¹⁷ Currie and Ramsay¹⁸ measured the absorption spectrum of the allyl radical in the 410–370 nm region. A system of diffuse bands in that region were assigned to the $\tilde{\text{A}}(1^2B_1) \leftarrow \tilde{\text{X}}(^2A_2)$ electronic transition. Other vibronic bands have also been de-

tected in the 210–250 nm region.¹⁹ Oscillator strengths of several UV bands have been measured experimentally.^{20,21} The resonant multiphoton ionization (MPI) technique was used to probe the one-photon forbidden transition $\tilde{\text{B}}(3s^2A_1) \leftarrow \tilde{\text{X}}(^2A_2)$ ^{22,23} with a (2+2) scheme. Three fundamental vibrational levels in both the ground and excited states were identified. Recently Chen and co-workers reported an extensive high resolution spectroscopic study on this radical.^{24–26} They have produced a supersonic molecular beam of allyl radical by flash pyrolysis²⁷ of allyl iodide. From their partially rotationally resolved MPI spectra they were able to assign many vibronic bands in the 250–240 nm region and to deduce the band origins of the strongly interacting $\tilde{\text{B}}(3s^2A_1)$, $\tilde{\text{C}}(2^2B_1)$, and $\tilde{\text{D}}(1^2B_2)$ electronic states.

Several theoretical studies at different levels of calculations have analyzed the ground-state structure and vibrational frequencies.^{28–34} The *ab initio* molecular orbital–configuration interaction (MO–CI)³⁵ and spin-coupled valence-bond (SCVB)³⁶ methods have also been used to study the ground and excited electronic states of the allyl radical. The energies of the excited electronic states were obtained, which are in good agreement with the experimental results.^{18,25}

Another interesting aspect of the allyl radical is the possible isomerization into cyclopropyl radical through an electrocyclic reaction.^{37–39} From the Woodward–Hoffmann rules,⁴⁰ based on MO symmetry considerations, both conrotatory and disrotatory pathways are symmetry forbidden on the ground-state potential energy surface, so that the ground state of each radical correlates with an electronically excited state of the other.⁴¹ However, the thermal ring opening of cyclopropyl radical into allyl radical has been observed ex-

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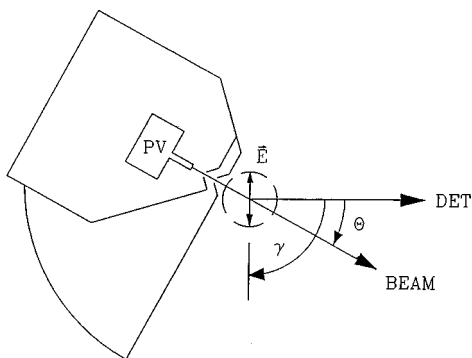


FIG. 1. Schematic view of the apparatus. Photolysis laser is perpendicular to the plane of the figure. PV, pulsed valve; DET, detector; E, direction of the electric vector of the laser. The polarization angle γ is defined with respect to the detector axis as shown, and the laboratory scattering angle Θ is the angle between the molecular beam and the detector axis.

perimentally and the activation energy was estimated to be about 20 kcal/mol.⁴² This result also agrees with an *ab initio* calculation³⁹ in which a highly nonsymmetrical transition state was found.

Very recently Deyerl *et al.*⁴³ have investigated the photodissociation of the allyl radical at 248.15 nm. The H-atom loss channel has been detected, showing an average translational energy release of 13.9 kcal/mol. Despite all the experimental and theoretical studies described above, a full picture of the primary photochemical processes of the allyl radical is still lacking. In the present work, we report a study on the photodissociation of the allyl radical at 248 and 351 nm excitation by photofragment translational spectroscopy (PTS).

II. EXPERIMENT

The experimental measurements in this work were carried out on a rotating source photofragment-translational spectrometer which has been described previously in detail.^{44,45} A simple schematic drawing of the experimental setup is shown in Fig. 1. A pulsed molecular beam of the allyl radical (C_3H_5) seeded in helium was skimmed twice before entering the main chamber, where it was crossed at 90° with a focused pulsed laser beam. Neutral photofragments scattered from the laser-molecular beam interaction region and which fly along the detector axis are ionized by an electron bombardment ionizer at a distance of 36.7 cm from the interaction region. The ions produced in the ionizer are then mass selected by a quadrupole mass spectrometer, and counted with a Daly ion detector. A 486 personal computer interfaced multichannel scaler (Turbo-MCS, EG&G Ortec) triggered by the laser pulse is used to collect and store the time-of-flight (TOF) spectra. Product laboratory angular distributions can be obtained by rotating the molecular beam source around the laser propagation axis, which is perpendicular to the plane defined by the molecular beam direction and the detector axis. The allyl radical pulsed beam was generated from the pyrolysis of allyl iodide (C_3H_5I). The pyrolytic source used in this experiment (Fig. 2) is an adaptation to our pulsed valve⁴⁶ of the one designed by Chen *et al.*²⁷ A mixture of $C_3H_5I/He \sim 0.2\%$ was expanded at a stagnation pressure of 760 Torr through a resistively heated

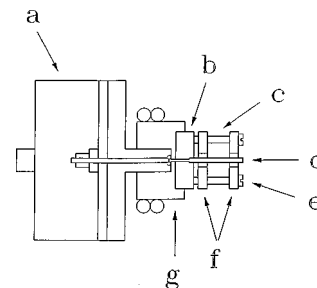


FIG. 2. Pyrolytic free radical pulsed molecular beam source. (a) pulsed valve, (b) alumina insulator block, (c) alumina standoff, (d) SiC tube, (e) alumina screws, (f) electrodes, (g) water cooled copper block.

SiC tube held at 1400–1500 K as determined by beam TOF. Under these conditions, C_3H_5I pyrolyses quantitatively to produce an allyl radical and iodine atom. The mass spectra of the molecular beam with the nozzle unheated (upper trace) and heated (lower trace) are shown in Fig. 3. The quantitative loss of C_3H_5I ($m/e=168$) and the appearance of I^{++} peak ($m/e=63.5$) in the heated mass spectrum are strong evidence for the formation of the allyl radical, since doubly charged ions are much more likely to come from one atom than from the dissociative ionization of C_3H_5I . The molecular beam velocity and its velocity spread were measured by the time-of-flight technique with a spinning slotted disk. Different parts of the gas pulse can be sampled by changing the delay between the wheel and the pulsed valve so that optimum experimental conditions are achieved. The delay between the pulsed valve and the laser trigger can be calculated from the wheel angular velocity and the delay between the pulsed valve and the wheel. The beam velocity was measured to be ~ 3300 m/s with a full width half-maximum (FWHM) velocity spread of 17%.

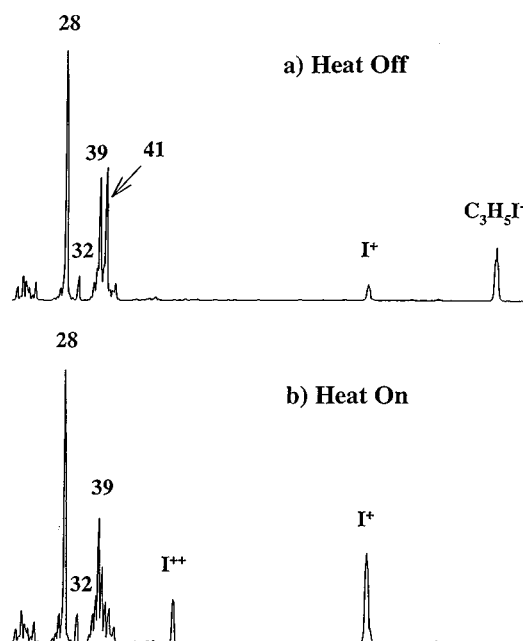


FIG. 3. Mass spectra of the molecular beam of $\sim 0.2\%$ allyl iodide in He taken with the pyrolytic nozzle at (a) room temperature (heat off) and (b) 1400 K (heat on).

In all the experiments performed in this work the molecular beam was crossed at 90° by an output of a Lambda Physik EMG 103 MSC excimer laser operating at the KrF (248) and XeF (351 nm) transitions. A convex lens (25 cm focal length) was used to focus the laser beam to a 2.5×6 mm spot in the interaction region, with fluence of 50–100 $\text{mJ}/\text{cm}^2/\text{pulse}$ for studies at 248 nm excitation and 100–200 $\text{mJ}/\text{cm}^2/\text{pulse}$ for studies at 351 nm excitation. The output of the excimer laser was polarized using a pile of ten quartz plates at Brewster's angle with respect to the direction of laser propagation, yielding $>95\%$ polarized light. The polarization direction of the laser beam can be rotated with respect to the detector axis by adjusting the orientation of the polarizer.

Time-dependent background, arising from the dissociative ionization of pulsed C_3H_5 from the molecular beam, was present in TOF spectra at masses ≤ 41 (C_3H_5) and at small angles. The shot-by-shot background subtraction method was used, which has been described in detail elsewhere.⁴⁷ Briefly, the pulsed valve was run at twice the laser repetition rate. A TOF spectrum with laser on and laser off was recorded, and the laser-off TOF was then subtracted from the laser-on TOF.

A forward convolution technique was used to fit the data. Briefly, a trial center-of-mass translational energy distribution is convoluted with the instrumental response functions to yield a calculated TOF spectrum in the laboratory reference frame, which is then compared to the experimental spectrum. The translational energy distribution is iteratively adjusted until a good fit is obtained.

At 248 nm excitation, the intensity of all detected fragments from C_3H_5 photodissociation varied linearly at lower laser power, but showed saturation at higher laser power. At 351 nm excitation, the intensity of C_3H_4 fragments (see below) varied linearly with the laser power up to the maximum power of the excimer laser, showing that the absorption cross section at this wavelength is quite small. The TOF spectra reported in this work have been recorded under conditions where saturation effects were absent.

H and D atoms produced in photodissociation experiments are difficult to detect by mass spectrometry for two main reasons. The signal is very low (kinematics factor) and the inherent background inside the detector at those masses is very high. The only way to increase the signal-to-noise ratio (S/N) is to increase the number density of the parent molecules by reducing the distance between the nozzle and the interaction region. H-atom TOF spectra have been measured with success in our group on several systems⁴⁸ but always on crossed molecular beam type machines⁴⁹ because of the space available in the fixed source chamber. We have slightly modified our experimental apparatus (also called "rotating source machine") in order to detect H-atom time of flight, the C_3H_4 momentum-matched photofragment. The modification was simply the addition of an extension to the source chamber (Fig. 4). In the modified setup, the pulsed valve is located upward inside this box. Two small holes exist along the laser beam propagation direction to let the laser beam pass through, and a third hole is present along the

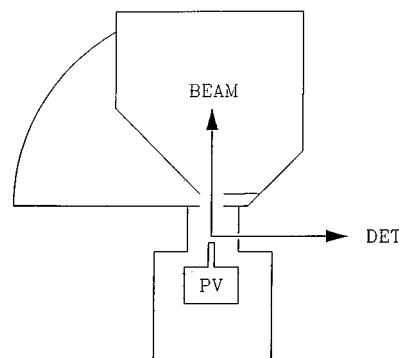


FIG. 4. Schematic view of the modified apparatus for H-atom detection. The photolysis laser is directed perpendicular to the plane of the figure. PV, pulsed valve; DET, detector. The molecular beam direction is perpendicular to the detector axis ($\Theta = 90^\circ$).

detector axis to let photofragments going to the detector pass. In this configuration the molecular beam, the laser beam, and the detector axis are all perpendicular to each other. The 1.5 mm diameter laser spot is located at a distance of 1 cm from the nozzle. While the H-atom detection was not successful for the allyl radical, owing to a low number density of the parent molecule, H-atom TOF spectra from the photodissociation of other systems were recorded.⁵⁰ Moreover, the same configuration was used to detect H and D atoms from the photolysis of HI and DI at 248 nm in order to determine experimentally the instrumental response functions (the ionizer width and the neutral flight distance) of our apparatus. In Fig. 5 the H- and D-atom TOF spectra from photodissociation of HI and DI at 248 nm excitation are shown. From the peak positions of the two spin-orbit components, the neutral flight distance (the bond dissociation en-

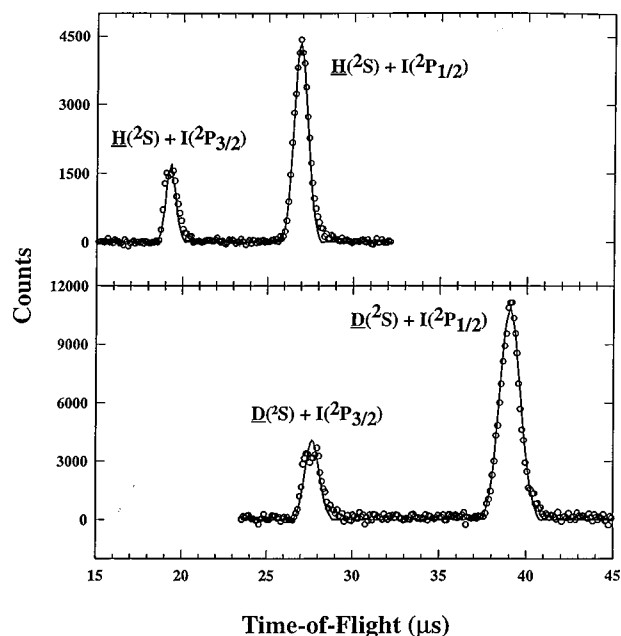


FIG. 5. TOF spectra at a laboratory angle of 90° for $m/e=1(\text{H}^+)$ and $m/e=2(\text{D}^+)$ from photodissociation of HI and DI at 248 nm. The open circles represent experimental data. The solid line is the calculated TOF from the convolution on the instrumental response functions of the experimental apparatus (neutral flight length, 36.7; ionizer width, 0.9 cm).

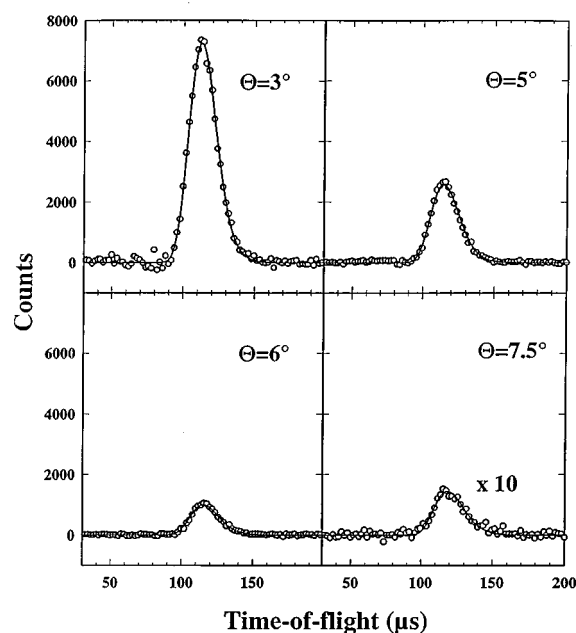


FIG. 6. TOF spectra for m/e 38 ($C_3H_2^+$) from photodissociation of the allyl radical at 248 nm at the indicated laboratory angles. The open circles are experimental points and the solid line is the simulation using the $P(E_T)$ in Fig. 7.

ergy, D_0 , of the two channels is well known⁵¹) is determined to be 36.7 cm, and from the widths of the two peaks the ionizer width can also be determined to be 0.9 cm.

III. RESULTS AND ANALYSIS

In all the TOF spectra presented here, the open circles represent the experimental data, the dashed lines are single channel contributions to the forward convolution fit, and the solid lines are the overall fit to the data. The lowest energy range of the $P(E_T)$ distributions are not reported because those that are very slow are not scattered beyond 2.5° from the molecular beam.

A. 248 nm excitation

At 248 nm excitation two primary dissociation channels are present (see below). For the H-atom loss channel, TOF spectra were collected for products at $m/e=41-38$ ($C_3H_5^+$, $C_3H_4^+$, $C_3H_3^+$, $C_3H_2^+$) at detector angles, Θ , of 2.5° , 3° , 4° , 5° , 6° , and 7.5° from the molecular beam. TOF spectra at $m/e=41$ were recorded in order to check if the signal observed at lower masses came from the photodissociation of the allyl radical or from heavier hydrocarbon molecules. The low signal at this mass ($\sim 2\%$ of $m/e=40$) is due only to ^{13}C natural abundance in C_3H_4 neutral fragments. TOF spectra at $m/e=40-38$ show a single peak and they are identical when recorded at the same laboratory angle, suggesting that they all originate from the same neutral fragment by electron impact dissociative ionization inside the ionizer. TOF spectra at $m/e=39$ and 38 have the best S/N. Figure 6 shows the TOF spectra for m/e 38 at $\Theta=3^\circ$, 5° , 6° , and 7.5° . The number of laser shots necessary for each spectrum ranged from 25 000 (at small Θ) to 100 000 (at larger Θ). The center-of-mass (c.m.) translational energy distribution, $P(E_T)$, used to fit

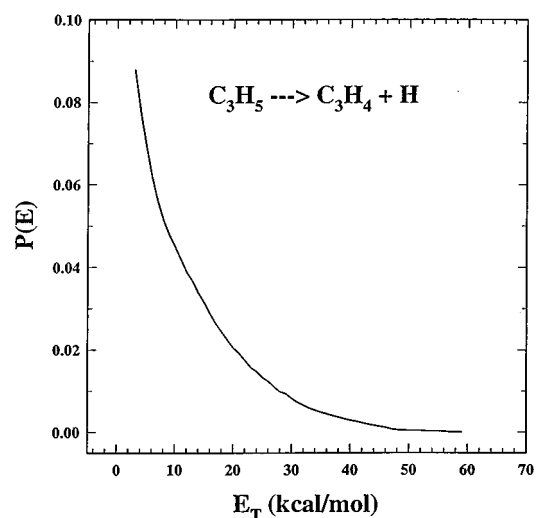


FIG. 7. The center-of-mass translational energy distribution used to fit the data in Fig. 6.

these TOF spectra is shown in Fig. 7. It is peaked around 0 and has a tail that decreases monotonically up to 59 kcal/mol. The mean translational energy release, $\langle E_T \rangle$, for this channel is 13.2 kcal/mol and represents an upper limit for the reasons mentioned before.

For the $CH_3+C_2H_2$ channel, both momentum-matched photofragments have been detected. TOF spectra for m/e 26 ($\Theta=7.5^\circ$, 15° , 20° , 25° , and 30°) and 15 ($\Theta=30^\circ$) have been collected after 300 000 (m/e 26) and 1 500 000 (m/e 15) laser shots. In Fig. 8, the TOF spectra collected for m/e 26 at 7.5° , 15° , 20° , and 30° are presented. At $\Theta=7.5^\circ$, two different peaks, centered around 80 and $120 \mu s$, are clearly resolved. At larger Θ only one single peak is present. The Newton

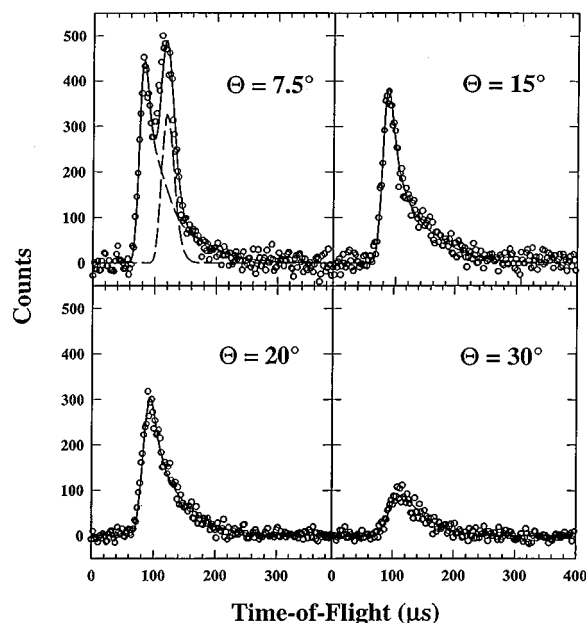


FIG. 8. TOF spectra for $m/e=26$ ($C_2H_2^+$) from photodissociation of allyl radical at 248 nm at the indicated laboratory angles. The open circles are experimental points, the dashed line is the contribution from the $C_2H_2+CH_3$ channel, the dotted line is the contribution from the C_3H_4+H channel, and the solid line is the total fit to the data.

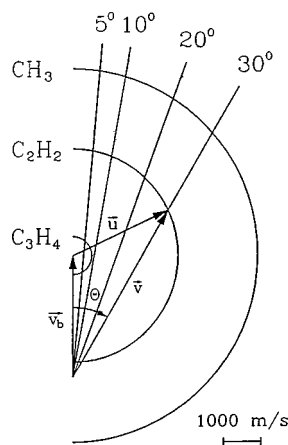


FIG. 9. Newton diagram for allyl radical photodissociation at 248 nm. The circles represent the thermodynamic limit for each photofragment.

diagram is shown in Fig. 9, with circles representing the highest possible velocities of the photofragments when all the available energy is channeled into translation. For the H-atom loss channel, the C_3H_4 product can be allene and/or methylacetylene (see Sec. IV). It is clear from the comparison with TOF of C_3H_4 that the slow component in the TOF at $m/e=26$ and 7.5° is due to C_3H_4 dissociative ionization and its contribution can be fitted with the $P(E_T)$ shown in Fig. 7. The $P(E_T)$ used to fit the acetylene channel is shown in Fig. 10. It has a totally different shape as compared to the H-atom loss channel. It is peaked at 16, $\langle E_T \rangle \sim 19.1$, with a FWHM of 20.5, and extends up to 62.0 kcal/mol. The same $P(E_T)$ has also been used to fit the TOF spectrum at $m/e=15$ (Fig. 11), showing that it is the momentum-matched counterpart of acetylene.

In order to determine the branching ratio, R , between the two primary dissociation channels, the TOF spectrum at $m/e=26$ and 7.5° was used because both contributions were recorded under the same experimental conditions. R was calculated according to Eq. (1),⁵² where σ_a^o and σ_b^o are the

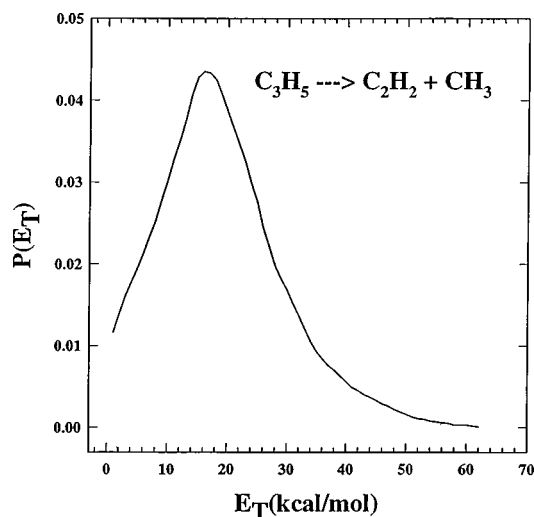


FIG. 10. The center-of-mass translational energy distribution used to fit the contribution of $C_2H_2+CH_3$ photodissociation channel in Figs. 8 and 11.

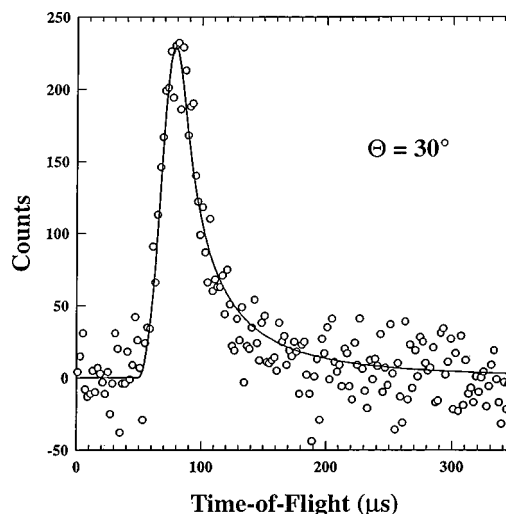


FIG. 11. TOF spectrum for m/e 15 (CH_3^+) from photodissociation of the allyl radical at 248 nm excitation at $\Theta=30^\circ$. The open circles are experimental points and the solid line is the simulation using the $P(E_T)$ in Fig. 10.

relative cross sections of fragments a and b monitored at a given m/e ratio and corrected for kinematics,

$$R = (\sigma_a / \sigma_b) = (\sigma_a^o / \sigma_b^o) (Q_b / Q_a) (F_b / F_a). \quad (1)$$

Q_a and Q_b are the ionization cross sections of the products which result in fragment a and b and were calculated using the method of Fitch and Sauter.⁵³ F_a and F_b are the probabilities of products in the ionization process to form fragments a and b at the given m/e ratio. We estimate the uncertainty in the branching ratio obtained in this way to be $\pm 25\%$. The ratio σ_a^o / σ_b^o (calculated by our analysis program) depends on the anisotropy parameter β , even if unpolarized light is used.⁵⁴ Polarization dependence studies were done for $m/e=38$, $\Theta=4^\circ$, and $m/e=26$, $\Theta=20^\circ$. The polarization direction of the light can be rotated in the plane defined by the molecular beam and the detector axis. The anisotropy parameter is obtained directly from the laboratory angular distribution⁵⁵ $I(\gamma)$,

$$I(\gamma) \propto 1 + \beta P_2(\cos(\gamma - \gamma_0)),$$

where γ is the laboratory polarization angle, γ_0 is the correction angle for the c.m. to laboratory transformation, and $P_2(\gamma - \gamma_0)$ is the second Legendre polynomial in $\cos(\gamma - \gamma_0)$. For the acetylene plus methyl (CH_3) channel we did not observe any dependence of the angular distribution from the polarization angle, indicating that this dissociation process is isotropic ($\beta=0$). For the H-atom loss channel, a very small negative anisotropy parameter β , -0.05 ± 0.02 , was observed. The branching ratio between the H-atom loss channel and the acetylene plus methyl channel at 248 nm excitation is determined to be 0.84:0.16.

B. 351 nm excitation

At the 351 nm excitation, only the H-atom loss channel was observed. TOF spectra were recorded for $m/e=40-38$ at detector angles of $2.5, 3, 4, 5$, and 6° from the molecular beam. Modulated background was also subtracted shot by shot. At 351 nm the available energy for the same asymptotic

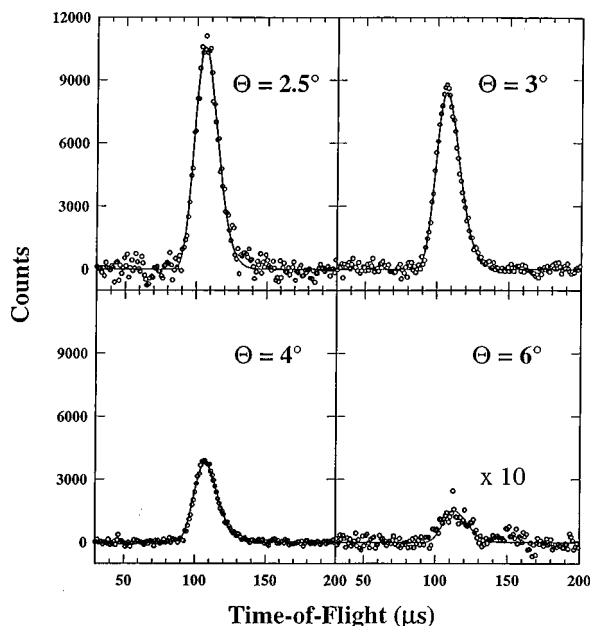


FIG. 12. TOF spectra for m/e 39 ($C_3H_3^+$) from photodissociation of the allyl radical at 351 nm at the indicated laboratory angles. The open circles are experimental points and the solid line is the simulation using the $P(E_T)$ in Fig. 13.

products is 33.5 kcal/mol lower as compared to 248 nm. The Newton circle will be smaller and the neutral C_3H_4 photo-fragments can be scattered only up to 6° from the molecular beam. TOF spectra obtained here show only a single peak, and they are identical for different m/e values when collected at the same laboratory angle. In Fig. 12, TOF spectra at $m/e = 39$ and $\Theta = 2.5, 3, 4$, and 6° are shown. The number of laser shots necessary for each spectrum ranges from 200 000 to 400 000. The c.m. translational energy distribution used to fit these TOF spectra is shown in Fig. 13. It has a similar shape as compared to the H-atom loss $P(E_T)$ at 248 nm. It peaks near 0 and decreases monotonically up to 24.5 kcal/mol. The upper limit for the mean translational energy release at 351 nm excitation is determined to be $\langle E_T \rangle$

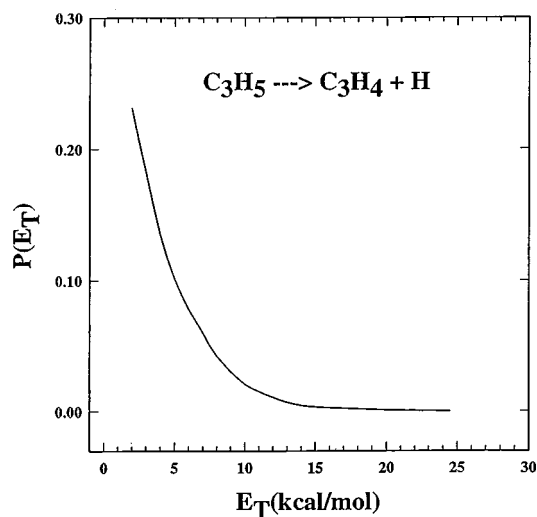


FIG. 13. The center-of-mass translational energy distribution used to fit the data in Fig. 12.

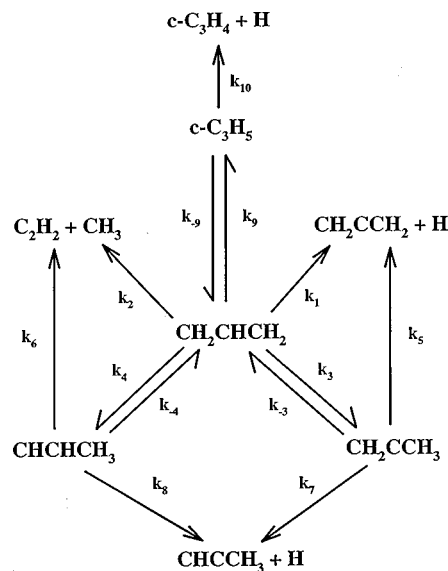


FIG. 14. Dissociation and isomerization reaction schemes. Also indicated are the unimolecular rate constants calculated by RRKM theory (cf. Table I).

$= 4.5$ kcal/mol. The anisotropy parameter measured for this channel was zero. Given the good signal-to-noise ratio for the TOF's and their simulation, the uncertainty in $\langle E_T \rangle$ is estimated to be less than 0.5 kcal/mol at both 351 and 248 nm.

C. RRKM calculations

In order to establish the relative importance of possible isomerization and dissociation reaction channels from the ground-state potential energy surface (PES) of the C_3H_5 system (see Sec. IV) we have performed RRKM calculation to determine the microcanonical rate constants $k(E)$'s for all the reaction pathways shown in Fig. 14. The lack of *ab initio* calculations at the same level of theory for all reaction pathways on the ground-state C_3H_5 PES required us to choose empirical methods to estimate vibrational frequencies and structures for the different radical species and transition states (TS's). The vibrational frequencies for the allyl radical have been taken from Refs. 10, 11, 13, and 34, for the cyclopropyl radical from Ref. 56. Vibrational frequencies for the 1- and 2-propenyl radicals were obtained from propylene removing one C–H stretch and two C–H bending vibrational modes. For k_1 , k_5 , k_6 , k_7 , k_8 , and k_{10} the TS's have been defined following the prescriptions given by Pearson and Rabinovitch.⁵⁷ TS's for the isomerization reactions among the allyl radical and the 1- and 2-propenyl radicals (through 1,3 and 1,2 H-atom migration, respectively) have been built in a similar way as Ibuki *et al.*⁵⁸ The TS for allyl-cyclopropyl isomerization (k_9, k_{-9}) was taken halfway. For the dissociation of allyl radical into $C_2H_2 + CH_3$ (k_2) through a four-member cyclic TS we have adopted a similar procedure used for k_3 and k_4 TS's with an additional lowering of CH_2 wagging, twisting, and rocking vibrations. In Table I, the calculated rate constants for 248 and 351 nm, together with energetic information and A-factors, are reported. Some of the isomerization and dissociation reactions have been

TABLE I. RRKM microcanonical rate constants, A -factors, excitation energies E , and zero-point energy differences E_0 between transition state and reactant^a for the reactions reported in Fig. 14.

Reaction	248 nm		351 nm		E_0 (kcal/mol)	log A
	$k(E)/10^{10}$ (s ⁻¹)	E (kcal/mol)	$k(E)/10^9$ (s ⁻¹)	E (kcal/mol)		
k_1	4.4	115.3	0.38	81.5	59.0 ^b	13.7
k_2	2.6	115.3	0.03	81.5	68.1 ^c	13.9
k_3	13.0	115.3	5.29	81.5	48.6 ^d	13.6
k_{-3}	32.6	103.2	17.4	69.7	36.8 ^d	13.1
k_4	3.9	115.3	1.62	81.5	49.8 ^e	13.4
k_{-4}	11.6	100.0	7.44	66.2	34.5 ^e	13.0
k_5	7.8	103.2	0.95	69.7	47.2 ^b	13.2
k_6	19.1	100.0	7.46	66.2	40.5 ^f	14.0
k_7	18.3	103.2	2.70	69.7	45.8 ^b	13.4
k_8	19.5	100.0	2.92	66.2	43.2 ^b	13.4
k_9	1.6	115.3	0.76	81.5	50.0 ^g	13.3
k_{-9}	70.3	87.2	115	53.4	21.9 ^g	13.3
k_{10}	1.1	87.2	0.00	53.4	52.9 ^h	13.7

^a ΔH_0 for reactants taken from Refs. 59 and 61.^bFrom Ref. 59 and references cited therein.^cA barrier of 20 kcal/mol for the reverse reaction is assumed (see text).^dFrom Ref. 66.^eFrom Ref. 58.^fFrom Ref. 64.^gFrom Ref. 39.^hA barrier of 3 kcal/mol for the reverse reaction is assumed.

investigated previously⁵⁹ with RRKM theory, and our results are in agreement with these results. In order to get branching fractions for the formation of allene, methylacetylene, cyclopropene, and acetylene, a set of differential equations for the reaction rates has been solved with the Laplace transform method,⁶⁰ and the results are listed in Table II. For the 248 nm case the initial condition in which only the allyl radical is present is reported here (assuming cyclopropyl radical as the initial molecular species present, the branching fraction values change less than one percentage unit, so that the global picture does not change).

The estimates of vibrational frequencies and structures made by empirical methods, and the use of the harmonic oscillator model to determine RRKM $k(E)$'s will certainly introduce some degree of error into the final branching fraction calculations. However, the qualitative picture given by these calculations is in agreement with our experimental results (see Sec. IV).

TABLE II. Branching fractions for the different dissociation channels calculated with the Laplace transform method (Ref. 60).

Reaction products	Branching fraction at 248 nm	Branching fraction at 351 nm
	39%	27%
$\text{CH}_2\text{CCH}_2 + \text{H}$	28% from CH_2CHCH_2 11% from $\text{CH}_2\text{C}\cdot\text{CH}_3$	17% from CH_2CHCH_2 10% from $\text{CH}_2\text{C}\cdot\text{CH}_3$
	34%	42%
$\text{CHCCH}_3 + \text{H}$	9% from $\cdot\text{CHCHCH}_3$ 25% from $\text{CH}_2\text{C}\cdot\text{CH}_3$	12% from $\cdot\text{CHCHCH}_3$ 30% from $\text{CH}_2\text{C}\cdot\text{CH}_3$
	27%	31%
$\text{C}_2\text{H}_2 + \text{CH}_3$	17% from CH_2CHCH_2 10% from $\cdot\text{CHCHCH}_3$	1% from CH_2CHCH_2 30% from $\cdot\text{CHCHCH}_3$
$c\text{-C}_3\text{H}_4 + \text{H}$	0.1%	0.0%

IV. DISCUSSION

A. Decay mechanisms at 248 nm

As mentioned above, Chen's group^{24–26} reported a detailed spectroscopic study of the allyl radical in the 240–250 nm region by resonant MPI. The band origin for the $\tilde{\text{C}}$ (2^2B_1) state was found to be 248.15 nm. The broadband KrF excimer laser used here certainly covers this transition. The absorption cross section increases at shorter wavelengths, reaching a maximum at ~ 222 nm.²¹ Several weaker and broader vibronic bands have also been observed at shorter wavelengths, implying a shorter lifetime for the excited state at the shorter wavelengths. The results of a gas-phase resonant Raman study at 225 nm are consistent with isomerization to cyclopropyl radicals.¹² In fact, the longer lifetime of the $\tilde{\text{C}}$ state at longer wavelengths could be due to the presence of a barrier for the electrocyclic transformation by a disrotatory mode.⁴¹ In this case the $\tilde{\text{C}}$ state decay could be through internal conversion (IC) to form vibrationally hot allyl radicals either in the ground state or in the $\tilde{\text{A}}$ state.⁴³ At shorter wavelengths, more rapid decay via isomerization to cyclopropyl is possible, provided sufficient energy is available to overcome the aforementioned barrier.

Following IC, allyl radical in the ground electronic state with 115.3 kcal/mol of vibrational energy can either dissociate or isomerize. A schematic energetic diagram with possible dissociation and isomerization processes is shown in Fig. 15. Thermochemical data have been taken from Refs. 59 and 61, and corrected to 0 K (see also Table I). There are two possible dissociation channels directly from an allylic structure: H-atom loss to form allene, reaction (R1), and CH_3 elimination through a concerted mechanism, reaction (R2). As mentioned above for the excited state, the allyl radical

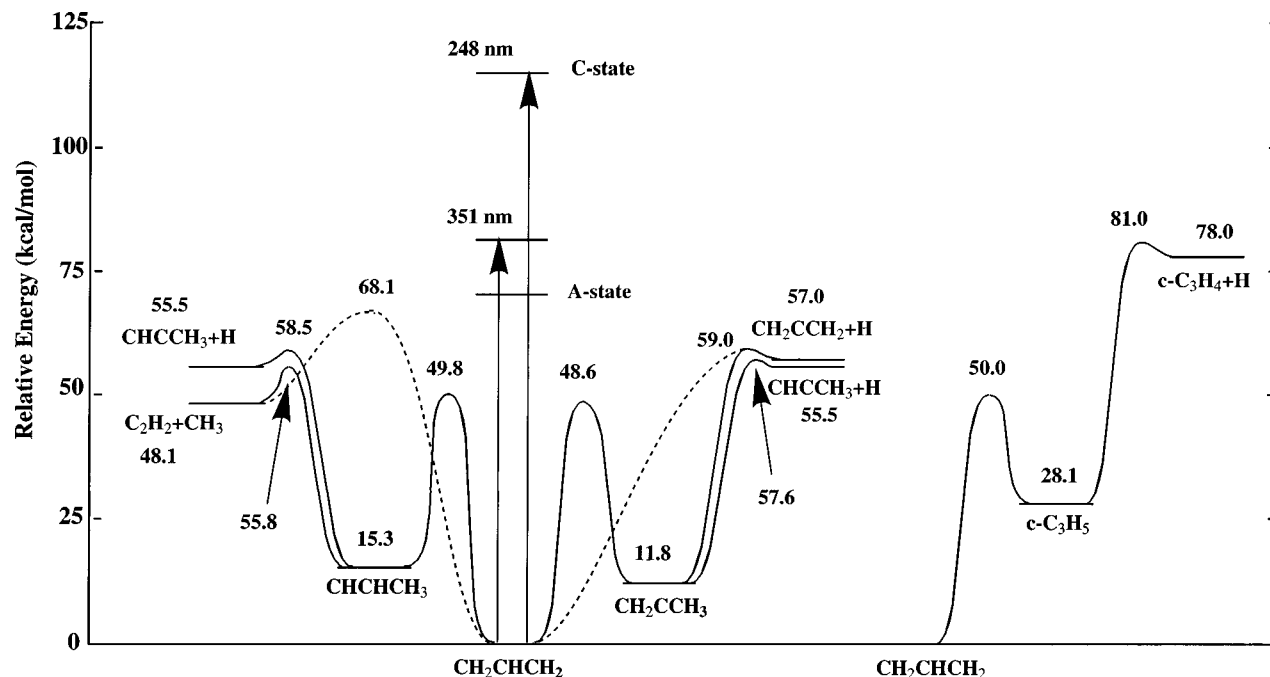
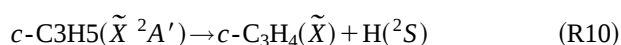
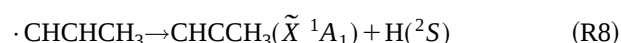
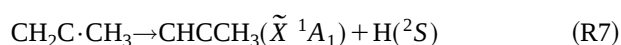
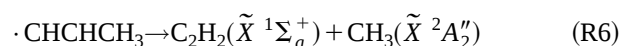
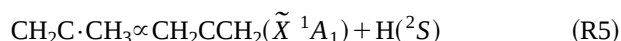
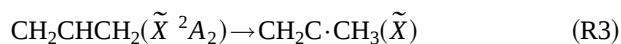
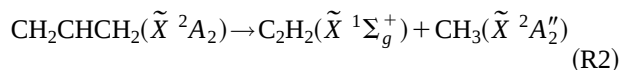


FIG. 15. Schematic diagram of the energetics of the allyl radical for the possible reaction channels following excitation at 248 and 351 nm. The numbers are relative energies (in kcal/mol) for different C_3H_5 isomers, transition states, and reaction products.

can isomerize by an electrocyclic transformation through a highly nonsymmetrical TS³⁹ into cyclopropyl radical, reaction (R9), or into 1- and 2-propenyl radicals through an H-atom shift, reactions (R4) and (R3), respectively. Finally, the cyclopropyl radical can lose an H-atom to form cyclopropene, reaction (R10); 1-propenyl radical ($\cdot CHCHCH_3$) can either lose the H-atom attached to the central carbon atom to form methylacetylene, reaction (R8), or can break the C–C bond to form C_2H_2 and CH_3 , reaction (R6); 2-propenyl radical ($CH_2C\cdot CH_3$) can lose an H-atom to form either methylacetylene, reaction (R7), or allene, reaction (R5). There are five different reaction pathways that produce an H-atom and allene/methylacetylene/cyclopropene, and two for the formation of acetylene plus the methyl radical,



B. The H-atom loss channel at 248 nm

The $P(E_T)$ for the H-atom loss channel (Fig. 7) is peaked near zero and extends up to the thermodynamic limit for allene/methylacetylene+H formation. This observation suggests that either or both molecular species may be formed as the final products. From the maximum E_T value it is not possible to establish if the less endothermic dissociation channel, CH_3CCH+H , is present. This is owing to the small difference (1.5 kcal/mol) between the enthalpy of formation (ΔH_0) of allene and that of methylacetylene. Cyclopropene is less stable than allene/methylacetylene by about 21–22 kcal/mol, therefore the available energy for reaction (R10) should be reduced by the same amount. This means that if this channel is present it should contribute at lower E_T . We do not observe any change of the slope of the $P(E_T)$ around the thermodynamic onset for this channel ($E_T \sim 37$ kcal/mol); moreover, the branching fraction obtained from RRKM calculations (Table II) is <1%. This low value is mainly due to the lower rate constant k_{10} for dissociation as compared to the isomerization reaction k_{-9} (Table I). The same RRKM calculations show that allene and methylacetylene are produced in almost equal amounts through an extensive isomerization before dissociation. More than 50% of the dissociation events do not come from allyl radicals directly. While the shape of the $P(E_T)$ is in qualitative agreement with a statistical dissociation, the mean translational energy release of 13.2 kcal/mol, in good agreement with what has been observed previously,⁴³ and a slightly negative anisotropy parameter are in apparent contradiction to the statistical dissociation picture. An RRKM type $P(E_T)$, which was calculated assuming no barrier on the exit channel, predicts an $\langle E_T \rangle$ of ~ 5 kcal/mol.⁶² Even if we assume that all the energy

from the potential barrier for the reverse reaction is channeled into translation, the predicted $\langle E_T \rangle$ will be only ~ 7 – 8 kcal/mol, still less than the experimental value.

The transition moment of the $\tilde{C}(2^2B_1) \leftarrow \tilde{X}(^2A_2)$ transition is perpendicular to the C_{2v} axis and in the molecular plane³⁵ (M_y -type transition). Prompt dissociation to form allene plus an H-atom from the ground-state geometry would yield $\beta = -1$. The anisotropy parameter β will tend to zero for a polyatomic dissociation process with its dissociation time much longer than the rotational period of the parent molecule. This kind of behavior is expected for dissociation processes occurring from the ground electronic state following internal conversion from an electronically excited state. The higher $\langle E_T \rangle$ value found experimentally and the slightly negative β may be due to a competition between two different microdissociation mechanisms: internal conversion and predissociation through an excited electronic state. In this case, the anisotropy distribution measured should come from two different contributions, one nearly isotropic ($\beta = 0$) and another with $\beta < 0$. For the allyl radical, the only rotation that can change the angle between the initial direction of the transition moment and the final direction of the C–H bond, prior to bond scission, is around the axis perpendicular to the molecular plane. The classical rotational period around this axis, assuming a rotational temperature of 150 K, is 4.2 ps. From the partially rotationally resolved spectra we have estimated a lifetime for the $\tilde{C}$ state at 248 nm of 1–2 ps. This shows that predissociation should be faster than the rotational period showing up in a substantial negative value of β for the dissociation process. The low measured value of the anisotropy thus signifies the importance of the IC process at 248 nm.

Internal conversion of the $\tilde{C}$ state to the first low lying electronic excited $\tilde{A}(1^2B_1)$ state will produce allyl radicals with 11.4 kcal/mol of vibrational energy. Currie and Ramsay¹⁸ observed a number of diffuse vibronic bands in the 410–370 nm region, which were assigned to the $\tilde{A}(1^2B_1) \leftarrow \tilde{X}(^2A_2)$ transition. The resolution of their spectrophotometer was high enough to resolve rotational structures¹⁸ and they concluded that predissociation, to form allene plus an H-atom, could be responsible for the diffuseness of those bands. Irradiation of allyl radicals trapped in an Ar matrix with 410 nm light was shown to produce new vibrational bands in the IR spectrum assigned to the cyclopropyl radical.⁵⁶ The orbital correlation diagram for the interconversion of allyl and cyclopropyl radicals^{40,41} shows that the $\tilde{A}$ state of the allyl radical correlates with the ground state of the cyclopropyl radical along the conrotatory mode, suggesting that the ring closure process will be fast (symmetry allowed). This conclusion is also supported by *ab initio* calculations at the CASSCF level.⁶³ The main result of this calculation shows that the conrotatory pathway has no barrier along the reaction coordinate, and the disrotatory pathway has a barrier less than 1.5 kcal/mol. Their conclusion was that the cyclization process would be facile. They thus argued that this cyclization, rather than predissociation, was responsible for the diffuse character of the vibronic bands of the first absorption transition. As mentioned above, by

changing the initial conditions for the solution of the set of differential equations, with the cyclopropyl radical as the only molecular species initially present instead of the allyl radical, the global picture will not change. The only small difference is that the branching fraction for reaction (10) rises to 1%.

C. The methyl+acetylene channel at 248 nm

The second primary dissociation channel detected at 248 nm excitation is the formation of acetylene and the methyl radical. This accounts for 16% of the total dissociation events. In the studies on the thermal decomposition of the allyl radical,⁵⁹ the formation of acetylene has been observed, and was supposed to come only from 1-propenyl radical dissociation, reaction (R6). The barrier for the CH_3 addition reaction to C_2H_2 to form 1-propenyl radical has been found to be 7.7 kcal/mol.⁶⁴ This also represents the barrier on the exit channel for the reverse reaction. The upper limit for the most probable E_T for the dissociation of 1-propenyl into acetylene and CH_3 can be estimated to be about 7.7 kcal/mol, assuming that all the potential energy barrier is channeled into translation. However, our $P(E_T)$ for this is peaked at 16 kcal/mol (Fig. 10), much larger than the maximum expected for decomposition of the 1-propenyl radical. Our $P(E_T)$ thus suggests the existence of a tighter TS for this dissociation channel. A possible candidate for this transition state is a four-member cyclic TS, where one CH_2 group is rotated by about 90° . Dissociation of the allyl radical can occur through reaction (R2), where C_2H_2 and CH_3 are produced directly from the allyl radical through this four-member cyclic TS. The proposed TS structure is similar to the one for H_2 elimination reaction from ethylene where the $P(E_T)$ was found to be peaked at 20 kcal/mol.⁶⁵ The $P(E_T)$ peak position represents a lower limit to the potential energy barrier height. The asymmetry of the TS for reaction (R2) will couple efficiently the reaction coordinate with the other internal degrees of freedom, suggesting that the true barrier will be consistently higher and the products should be rotationally and vibrationally excited. The total branching fraction for this channel obtained from RRKM calculations (Table II) is 27%, higher than the value, 16%, determined experimentally. Moreover, 10% of the 27% fraction is due to reaction (6) according to the RRKM calculations. Even though the TOF spectra at $m/e = 26$ (Fig. 8) and the $P(E_T)$ do not show any bimodality, a contribution from reaction (R6) can still be present, especially at low E_T . We have simulated TOF spectra with two different contributions, one with a $P(E_T)$ peaked at 16 for reaction (R2) and the other peaked at ~ 5 kcal/mol for reaction (R6). Although this simulation procedure has a certain degree of arbitrariness, it shows that the contribution of reaction (R6) will likely be less than 15%–20% of the total for this channel, which is still somewhat lower than the calculated value. The contribution of reaction (R6) from the RRKM calculations can be lowered by increasing the barrier for the isomerization between the allyl and 1-propenyl radicals and/or choosing a tighter TS for reaction (R6). The branching fractions reported in Table II have been calculated by considering only statistical dissociation reactions from the

ground potential energy surface, therefore they do not include a possible contribution to the H-atom loss channel from predissociation. The higher branching fraction for the acetylene channel, as compared to the experimental value, may be due to the fact that the barrier assumed for reaction (R2) is too low in the RRKM calculations (20 kcal/mol). The dissociation products will be internally extremely hot, since on average about 77% of the available energy for the H-atom loss channel will be deposited to internal excitation (mainly vibrational excitation), and about 72% of the available energy remains in internal degrees of freedom for the acetylene plus CH₃ channel.

D. 351 nm dissociation

The absorption of a 351 nm photon excites the allyl radical to the $\tilde{A}(1^2B_1)$ state. The $\tilde{A}$ state decays through an electrocyclic transformation to the ground state of the cyclopropyl radical with 53.4 kcal/mol of vibrational energy. The absence of angular anisotropy ($\beta=0$), a $P(E_T)$ peaked around zero, and a mean translational energy of 4.5 kcal/mol are all consistent with this mechanism for the H-atom loss channel. In fact, a subpicosecond predissociation process to form allene plus an H-atom will show up with a negative β (the $\tilde{A}$ state has the same symmetry as the $\tilde{C}$ state). An RRKM type $P(E_T)$ for reactions (R1), (R8), (R7), and (R5), which are assumed barrierless, predict a $\langle E_T \rangle = 2.5$ kcal/mol. If we add ~ 2 kcal/mol for the repulsive interaction due to the small exit barrier, the agreement with the experimental value is very good. The threshold for the formation of cyclopropene plus an H-atom, reaction (R10), is 49.9 kcal/mol. Assuming a barrier of 3 for the reverse reaction, the available energy to overcome this barrier is only 0.5 kcal/mol. The rate constant for reaction (10), k_{10} , will be so low (Table I) that cyclopropene formation will not compete with the isomerization into ground-state allyl radical through a nonsymmetrical TS, k_{-9} . RRKM calculations show that isomerization of the allyl radical with 81.5 kcal/mol vibrational energy is extensive. Only 18% of the dissociation products (Table II) come from an allylic structure. Methylacetylene is predicted to be the most abundant product with 42% yield, allene 27%, and acetylene 31% (with 30% from dissociation of the 1-propenyl radical). The inability to detect signal at $m/e=26$ may be due to different reasons. If the barrier to the isomerization between the allyl and the 1-propenyl radicals is higher, the branching fraction for the acetylene channel will then be reduced. From a comparison of the signal levels for $m/e=38-39$ at 248 and 351 nm, we can conclude that the absorption cross section of the allyl radical at 351 nm is ~ 100 times smaller than 248 nm, which is in agreement with previous results.³⁵ The kinematics also plays an important role. For the H-atom loss channel the signal of the heavy fragment is concentrated in only 6 deg in the laboratory reference frame, while the Newton circle for C₂H₂ extends up to 40 deg. Finally, for the 351 nm excitation the dissociation products will still be internally hot, since on average $\sim 82\%$ of the available energy will be channeled into C₃H₄ internal excitation (mainly vibrational excitation).

V. CONCLUSION

Photodissociation of the allyl radical has been studied by photofragment translational spectroscopy following excitation to the $\tilde{C}(2^2B_1)$ and $\tilde{A}(1^2B_1)$ states. At 248 nm excitation, two different primary channels have been detected: H-atom loss (84%) and CH₃ elimination (16%). The overall shape of the $P(E_T)$ for the H-atom loss channel suggests a statistical dissociation from the ground potential energy surface of the C₃H₅ system. The decay mechanism of the excited state is either through internal conversion into the ground state or internal conversion into the $\tilde{A}$ state followed by an electrocyclic transformation into the ground-state cyclopropyl radical and, finally, reopening of the ring to form the allyl radical in the ground state with 115.3 kcal/mol of vibrational energy. The small negative anisotropy parameter β and the higher mean translational energy release $\langle E_T \rangle$, as compared to an RRKM type calculated value, can be rationalized by the competition between two different decay mechanisms for the $\tilde{C}$ state: internal conversion and predissociation through a higher excited state. RRKM calculations show that almost 50% of allyl radicals dissociate to give allene plus an H-atom and acetylene plus CH₃, while the remaining radicals isomerize into 1- and 2-propenyl radicals before dissociation to form allene and methylacetylene plus an H-atom. The $P(E_T)$ for the acetylene plus CH₃ channel is peaked away from zero at 16 kcal/mol and is due mainly to dissociation from an allylic structure. This result, supported also by RRKM calculations, has been interpreted as dissociation from an allylic structure through a cyclic four-member transition state. A smaller contribution to this channel could also come from dissociation of the 1-propenyl radical.

The $\tilde{A}$ state of allyl radical is reached after excitation at 351 nm. The decay mechanism is again an electrocyclic transformation into the ground-state cyclopropyl radical, followed by a reopening of the ring to form the allyl radical in the ground state with 81.5 kcal/mol vibrational energy. RRKM calculations also show that isomerization into the 1- and 2-propenyl radical is extensive, with final production of methylacetylene and allene plus an H-atom.

ACKNOWLEDGMENTS

D.S. gratefully acknowledges the Consiglio Nazionale delle Ricerche (Italy) for a fellowship. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

¹W. Tsang, *Int. J. Chem. Kinet.* **10**, 1119 (1978).

²M. Weissman and S. W. Benson, *Prog. Energy Combust. Sci.* **15**, 273 (1989).

³R. E. Linder, D. L. Winters, and A. C. Ling, *Can. J. Chem.* **54**, 1405 (1976).

⁴R. N. Carter, A. B. Anton, and G. Apai, *J. Am. Chem. Soc.* **114**, 4410 (1992).

⁵J. C. Schultz and J. L. Beauchamp, *J. Chem. Phys.* **87**, 3587 (1983).

⁶R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **39**, 2147 (1963).

⁷M. J. McManus, R. W. Fessenden, and D. M. Chipman, *J. Phys. Chem.* **92**, 3778 (1988).

- ⁸E. Vajda, J. Tremmel, B. Rozsondai, I. Hargittai, A. K. Maltsev, N. D. Kagramanov, and O. M. Nefedov, *J. Am. Chem. Soc.* **108**, 4352 (1986).
- ⁹F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.* **100**, 3290 (1978).
- ¹⁰J. W. Huang and W. R. M. Graham, *J. Chem. Phys.* **93**, 1583 (1990).
- ¹¹G. Maier, H. P. Reisenauer, B. Rohde, and K. Dehnicke, *Chem. Ber.* **116**, 732 (1983).
- ¹²J. D. Getty, M. J. Burmeister, S. G. Westre, and P. B. Kelly, *J. Am. Chem. Soc.* **113**, 801 (1991).
- ¹³J. D. Getty and P. B. Kelly, *Chem. Phys.* **168**, 357 (1992).
- ¹⁴X. Liu, J. D. Getty, and P. B. Kelly, *J. Chem. Phys.* **99**, 1522 (1993).
- ¹⁵J. D. Getty, X. Liu, and P. B. Kelly, *J. Phys. Chem.* **96**, 10,155 (1992).
- ¹⁶J. D. Getty, X. Liu, and P. B. Kelly, *Chem. Phys. Lett.* **201**, 236 (1993).
- ¹⁷E. Hirota, C. Yamada, and M. Okunishi, *J. Chem. Phys.* **97**, 2963 (1992).
- ¹⁸C. L. Currie and D. A. Ramsay, *J. Chem. Phys.* **45**, 488 (1966).
- ¹⁹A. B. Callear and H. K. Lee, *J. Chem. Soc., Faraday Trans.* **64**, 308 (1968).
- ²⁰H. E. van der Bergh and A. B. Callear, *Trans. Faraday Soc.* **66**, 2681 (1970).
- ²¹N. Nakashima and K. Yoshihara, *Laser Chem.* **7**, 177 (1987).
- ²²J. W. Hudgens and C. S. Dulcey, *J. Phys. Chem.* **89**, 1505 (1985).
- ²³A. D. Sappey and J. C. Weisshaar, *J. Phys. Chem.* **91**, 3731 (1987).
- ²⁴D. W. Minsek, J. A. Blush, and P. Chen, *J. Phys. Chem.* **96**, 2025 (1992).
- ²⁵J. A. Blush, D. W. Minsek, and P. Chen, *J. Phys. Chem.* **96**, 10,150 (1992).
- ²⁶D. W. Minsek and P. Chen, *J. Phys. Chem.* **97**, 13,375 (1993).
- ²⁷D. W. Kohn, H. Clauberg, and P. Chen, *Rev. Sci. Instrum.* **63**, 4003 (1992); H. Clauberg, D. W. Minsek, and P. Chen, *J. Am. Chem. Soc.* **114**, 99 (1992); H. Clauberg and P. Chen, *ibid.* **113**, 1445 (1991).
- ²⁸S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.* **51**, 2528 (1969).
- ²⁹T. Takada and M. Dupuis, *J. Am. Chem. Soc.* **105**, 1713 (1983).
- ³⁰C. Cometta-Morini, T.-K. Ha, and J. F. M. Oth, *J. Mol. Struct.: THEOCHEM* **188**, 79 (1989).
- ³¹E. Fjogstad and M. Ystenes, *Spectrochim. Acta A* **46**, 47 (1990).
- ³²P. G. Szalay, A. G. Csaszar, G. Fogarasi, A. Karpfen, and H. Lischka, *J. Chem. Phys.* **93**, 1246 (1990).
- ³³F. Sim, D. R. Salahub, S. Chin, and M. Dupuis, *J. Chem. Phys.* **95**, 4317 (1991).
- ³⁴E. Hirota, *J. Mol. Struct.* **320**, 75 (1994).
- ³⁵T.-K. Ha, H. Baumann, and J. F. M. Oth, *J. Chem. Phys.* **85**, 1438 (1986).
- ³⁶J. M. Oliva, J. Gerratt, D. L. Cooper, P. B. Karadakov, and M. Raimondi, *J. Chem. Phys.* **106**, 3663 (1997).
- ³⁷L. Farnell and W. G. Richards, *J. Chem. Soc. Chem. Commun.*, 334 (1973).
- ³⁸P. Merlet, S. D. Peyerimhoff, R. J. Buenker, and S. Shih, *J. Am. Chem. Soc.* **96**, 959 (1974).
- ³⁹S. Olivella, A. Solé, and J. M. Bofill, *J. Am. Chem. Soc.* **112**, 2160 (1990).
- ⁴⁰R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* (Academic, New York, 1970).
- ⁴¹H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.* **87**, 2045 (1965).
- ⁴²G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.* **62**, 3338 (1966).
- ⁴³H.-J. Deyler, T. Gilbert, I. Fischer, and P. Chen, *J. Chem. Phys.* **107**, 3329 (1997).
- ⁴⁴A. M. Wodtke and Y. T. Lee, *J. Phys. Chem.* **89**, 4744 (1985).
- ⁴⁵A. M. Wodtke, Ph.D. thesis, University of California, Berkeley, 1986.
- ⁴⁶D. Proch and T. Trickl, *Rev. Sci. Instrum.* **60**, 713 (1989).
- ⁴⁷D. Stranges, X. Yang, J. D. Chesko, and A. G. Suits, *J. Chem. Phys.* **102**, 6067 (1995).
- ⁴⁸R. E. Continetti, B. A. Balko, and Y. T. Lee, *J. Chem. Phys.* **93**, 5719 (1990); *Chem. Phys. Lett.* **182**, 400 (1991); B. A. Balko, J. Zhang, and Y. T. Lee, *J. Chem. Phys.* **94**, 7958 (1991); D. A. Blank, S. W. North, and Y. T. Lee, *Chem. Phys.* **187**, 35 (1994).
- ⁴⁹Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, *Rev. Sci. Instrum.* **40**, 1402 (1968).
- ⁵⁰D. Stranges, A. G. Suits, and Y. T. Lee (unpublished results); D. A. Blank, S. W. North, D. Stranges, A. G. Suits, and Y. T. Lee, *J. Chem. Phys.* **106**, 539 (1997).
- ⁵¹H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978).
- ⁵²A. M. Schmoltner, Ph.D. thesis, University of California, Berkeley, 1989.
- ⁵³W. L. Fitch and A. D. Sauter, *Anal. Chem.* **55**, 832 (1983).
- ⁵⁴J. G. Frey and P. Felder, *Mol. Phys.* **75**, 1419 (1992).
- ⁵⁵G. E. Busch and K. R. Wilson, *J. Chem. Phys.* **56**, 3638 (1972); R. N. Zare, *Mol. Photochem.* **4**, 1 (1972).
- ⁵⁶K. Holtzhauser, C. Cometta-Morini, and J. F. M. Oth, *J. Phys. Org. Chem.* **3**, 219 (1990).
- ⁵⁷M. J. Pearson and B. S. Rabinovitch, *J. Chem. Phys.* **42**, 1624 (1965).
- ⁵⁸T. Ibuki, T. Murata, and Y. Takezaki, *J. Phys. Chem.* **78**, 2543 (1974).
- ⁵⁹J. Niedzielski, J. Gawłowski, and T. Gierczak, *J. Photochem.* **21**, 195 (1983); M. Naroznik and J. Niedzielski, *ibid.* **32**, 281 (1986).
- ⁶⁰J. I. Steinfeld, J. S. Francisco, and W. L. Hase, *Chemical Kinetics and Dynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1989).
- ⁶¹*CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC, Boca Raton, FL, 1992).
- ⁶²The RRKM type $P(E_T)$ calculated for the reactions (3), (9), (11), and (12) give the same $\langle E_T \rangle$ value.
- ⁶³M. Yamaguchi, *J. Mol. Struct.: THEOCHEM* **365**, 143 (1996).
- ⁶⁴J. A. G. Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962).
- ⁶⁵B. A. Balko, J. Zhang, and Y. T. Lee, *J. Chem. Phys.* **97**, 935 (1992); E. F. Cromwell, A. Stolow, M. J. J. Vrakking, and Y. T. Lee, *ibid.* **97**, 4029 (1992); A. Stolow, B. A. Balko, E. F. Cromwell, J. Zhang, and Y. T. Lee, *J. Photochem. Photobiol., A* **62**, 285 (1992).
- ⁶⁶Von B. Ondruschka, U. Ziegler, and G. Zimmermann, *Z. Phys. Chem. (Leipzig)* **267**, 1127 (1986).