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Photodissociation dynamics of ketene at 157.6 nm

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Photodissociation dynamics of ketene at 157.6 nm has been investigated using the photofragment translational spectroscopic technique based on photoionization detection using vacuum-ultraviolet synchrotron radiation. Three dissociation channels have been observed: CH_2+CO , CH+HCO, and HCCO+H. The product translational energy distributions and angular anisotropy parameters were measured for all three observed dissociation channels, and the relative branching ratios for different channels were also estimated. The experimental results show that the direct C–C bond cleavage (CH_2+CO) is the dominant channel, while H migration and elimination channels are very minor. The results in this work show that direct dissociation on excited electronic state is much more significant than the indirect dissociation via the ground state in the ketene photodissociation at 157.6 nm. © 2006 American Institute of Physics. [DOI: 10.1063/1.2147221]

I. INTRODUCTION

Ketene (CH₂CO) has received much attention in the field of photochemistry. It has been long known as the photochemical source of methylene radical in both interstellar space and in laboratory work. Moreover, ketene has proven to be a benchmark system for theoretical study of unimolecular dissociation.^{1,2} Photodissociation of ketene in a collisionfree environment has been investigated at 193 nm excitation³ and longer wavelengths.⁴⁻⁸ Both H atom elimination and C=C bond cleavage channels have been observed as major primary photodissociation pathways. Previous experimental results suggest that the H atom elimination channel at 193 nm excitation occurs on the ground electronic state surface and exhibits clear statistical signature, C=C bond fission process was the main focus of previous ketene photodissociation studies. Both triplet and singlet CH₂ radicals have been observed in this dissociation process. Previous studies indicate that $CH_2({}^1A_1)$ was produced by internal conversion from S_1 state to ground state (S_0), while the groundstate $CH_2({}^{3}B_1)$ radical is produced from intersystem crossing to the T_1 potential-energy surface after vertical excitation.

The vacuum-uv absorption spectrum of the ketene molecule has been measured previously. The electron transition around 157.6 nm was assigned to the $3 {}^{1}A_{1}(3d)-X {}^{1}A_{1}$ band.^{9,10} There are three lower 3*d* Rydberg states, $3 {}^{1}A_{1}$, $3 {}^{1}B_{1}$, and $3 {}^{1}A_{2}$. The transition to the lowest $(3 {}^{1}A_{1}) 3d$ Rydberg state has the largest oscillator strength. The theoretical calculations¹⁰ also show that the symmetry of the ketene in $3 {}^{1}A_{1}$ potential-energy surface is C_{S} -I symmetry (out-ofplane bent). Up until now, most photodissociation studies of ketene were focused on the diffuse absorption band region, to the $1 {}^{1}A_{2}$ and $1 {}^{1}B_{1}$ states.

In this work, ketene photodissociation at 157.6 nm excitation to the 3 ${}^{1}A_{1}$ electronic state was investigated. Several product channels are energetically accessible at 157.6 nm excitation (see Fig. 1). A molecular-beam apparatus based on synchrotron radiation as the ionization detection scheme was used this work. Time-of-flight spectra were obtained by the photofragment translational spectroscopy (PTS) technique. The product angular anisotropic parameter β for these channels was measured, and the relative branching ratio of different channels have also been estimated.

II. EXPERIMENT

The experimental apparatus and method are described in detail in a previous publication¹¹ and elsewhere.^{12–15} In order to understand the dissociation dynamics of ketene at 157.6 nm clearly, photofragment time-of-flight (TOF) spectra were measured in a molecular-beam apparatus with vacuum ultraviolet (vuv) ionization. The character of this apparatus is the tunable vuv photon beam to ionize the neutral photofragment in the ionization region of the detector. The tunable vuv photon beam comes from the U9 beamline of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The molecular-beam machine consists of three parts: the rotatable source, the reaction chamber, and the fixed detector. A pulsed molecular beam of 10% ketene seeded in Ar was made by expanding the sample from source chamber into the reaction main chamber with a backing pres-

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FIG. 1. Schematic energy diagram for the photodissociation channels of ketene at 157.6 nm (181.4 kcal/mol) excitation.

sure of 700 Torr. The molecular beam was intersected at 90° with a F₂ excimer laser (157.6 nm) beam, Lambda Physik LPF 220i F. In order to avoid the multiphoton dissociation effect, the 157.6 nm laser power was attenuated by one or two mesh screens to be about 0.5-1 mJ per pulse during the experiment. The vacuum pressure of the reaction chamber was maintained at 2×10^{-8} Torr evacuated by a 2000 1/s turbomolecular pump and a cryopump, thus a collision-free condition was achieved. After flying about 100 mm from the crossed region, the neutral reaction products were ionized by the tunable synchrotron vuv photon beam. For the sake of sufficiently ionizing the reaction products, we employed a windowless noble gas filter in the beamline to substitute for a monochromoator. The photon flux of tunable vuv beam is estimated to be about 10¹⁶ photon s⁻¹ and the spectrum energy resolution is about 3%. In this experiment, the synchrotron photon energy is tunable by adjusting the gap of the undulator device raging from 30 to 36 nm, corresponding to 11-17.5 eV. The ionization region was evacuated to less than 4×10^{-12} Torr with several turbomolecular pumps and a liquid-nitrogen-cooled trap. After ionization, the photofragment ions are focused by ion optics, mass selected by a quadrupole mass filter, and recorded with a Daly-type ion counter. The TOF spectra for different fragment from the photodissociation of ketene at 157.6 nm have been measured using the apparatus described above. To obtain a TOF spectrum with a good signal-to-noise ratio, the experimental TOF spectra were taken by averaging over about $\sim 5 \times 10^5$ laser shots. The measurement of angular anisotropy of products has been carried out in the photolysis of ketene at 157 nm. In this experiment, the TOF spectra for different products at different laser polarizations are measured using a thin-film polarizer (Laseroptik GmbH). The polarizer setup is described in detail elsewhere.^{1,16}

Ketene (CH₂CO) was synthesized according to literature procedures through thermal decomposition of acetic anhydride (Aldrich 99%) at temperature $\sim 800 \text{ K.}^{17}$ The ketene thus formed was collected using a liquid nitrogen bath at 77 K; most of the by-product such as acetic acid was trapped at 185 K using a dry ice/methanol slush before entering the sample collector. The reaction products were then purified using vacuum distillation from 195 to 77 K several times to remove impurities such as CO_2 and CH_3COOH .

The product TOF spectra from photodissociation of the ketene compounds were measured in the laboratory frame. In order to obtain the center-of-mass translational energy distributions $P(E_T)$, the analysis of the laboratory TOF spectra was performed using a forward convolution program, PHOT-RAN. In this computer program, the spectra of two momentum matched fragments produced in a binary dissociation process can be simulated using a translational energy distribution $P(E_T)$.

III. RESULTS AND DISCUSSIONS

In this experiment, TOF spectra of the products produced in the photodissociation of ketene at 157 nm were measured using vuv photoionization technique. Signals of the photodissociation products from ketene photolysis at mass $13(CH^+)$, $14(CH_2^+)$, $28(CO^+)$, $29(HCO^+)$, and $41(HCCO^+)$ have been detected. After careful measurement and detailed analyses of the TOF spectra, three dissociation channels were identified: the CH₂+CO channel, the CH +HCO channel, and the HCCO+H channel. Anisotropy parameters have also been determined for all observed photofragments.

A. CH₂+CO channel

Figure 2 shows the TOF spectra of mass $14(CH_2^+)$ and mass $28(CO^+)$ from the photodissociation of ketene at 157.6 nm. In the TOF spectra of mass 14, no significant dissociative ionization was observed by tuning the detection photon energy from the ionization threshold to 14 eV. The TOF spectra at mass 14 and mass 28 at 30° can be easily simulated using a single kinetic-energy distribution, indicating that products are momentum matched and from a single binary channel. The translational energy distribution $P(E_T)$ is shown in Fig. 3(a). These two TOF spectra can be assigned to the CH₂+CO channel.

Figure 4 shows the TOF spectra of CH_2 and CO detected using dissociating light with polarization parallel and perpendicular to the TOF axis. The angular anisotropy parameter β



FIG. 2. (a) The TOF spectra of mass 28 product at the laboratory angle of 30° using 14.5 eV photon energy. Curve 1 is the contribution from CH₂ +CO channel. Curve 2 was simulated by dissociation ionization from the HCO radical. (b) TOF spectra of mass 14 at the laboratory angle of 30° using 12.8 eV photon energy. The opened circles are the experimental data points, while the solid lines are the simulated contributions.

is about 0.7 near the peak. It is clear that the angular anisotropy parameter is translational energy dependent. The slower part of the signal is from the HCO channel, the anisotropy of this channel is clearly zero. The seemed energy dependence of β could be partly from the overlapped signals between the CH_2+CO channel and the HCO+CH channel. In addition, the direct dissociation of CH₂+CO could also exhibit an energy-dependent angular anisotropy as in many other cases.¹⁸ If direct bond dissociation coupled with an angular motion, it is possible that product angular anisotropy is strongly energy dependent. Photodissociation of ketene in this channel with 193 nm has been previously studied by Fujimoto et al.¹⁹ and Sonobe and Rosenfeld.²⁰ Their study indicated clearly that CO product is highly vibrationally and rotationally excited, since dissociation process via a nonlinear geometry. In this case, the energetic limit of the product translational energy distribution is consistent with the limit of the $CH_2({}^{1}B_1) + CO({}^{1}\Sigma^+)$ channel. The dissociation process is spin allowed since the initially excited state is also a singlet state. The average product translational energy, $\langle E_T \rangle$, is about 36% of the total available energy for this channel. This is consistent with the theoretical calculations that the initial excitation is to the 3 ${}^{1}A_{1}$ state, a diffusive Rydberg state that is likely coupled to a direct dissociative state. A positive β parameter for this channel also supports this picture. Since



FIG. 3. (a) The translational energy distribution $P(E_T)$ of CH₂+CO channel. (b) $P(E_T)$ of CH+HCO channel. The error bars for the two distributions are about ±10%.

the anisotropy parameter is positive, suggest that transition dipole moment should be parallel to the C–C–O plane. It is also clear that the lifetime of this dissociating molecule is not sufficiently long to smear the angular anisotropy parameter totally. Quite likely, the dissociation time should be comparable to the rotational time of the parent molecule.

B. CH+HCO channel

The TOF spectra at mass $13(CH^+)$ and mass $29(HCO^+)$ have also been observed at a laboratory angle of 30°, as shown in Fig. 5. As we can see in Fig. 5(a), the fast curve 1 is attributed to the contribution from the ¹³C of CO molecule (m/e=29). Another slower curve 2 can be assigned to the CH+HCO channel signal. This component can be momentum matched with the slower part (curve 2) of the TOF spectrum at mass 13 [Fig. 5(b)] using the same kinetic-energy distribution shown in Fig. 3(b). There are three distinct features in the TOF spectra of mass 13 shown in Fig. 5(b). The small and fast peak (curve 1) is attributed to the dissociative ionization of CH₂ product. This peak could be fitted using the kinetic-energy distribution shown in Fig. 3(a). In addition, the slowest part (curve 3) is clearly from the cracking of mass 41 product (HCCO) from the H atom elimination that will be discussed later.

Since the energy of this channel is quite high, \sim 173.4 kcal/mol, this channel only opens up at very high excitation energy. The available energy for this dissociation



FIG. 4. Upper panel: TOF spectra of mass 28 (CO) product at θ =30° measured at two different photolysis polarization direction using 15.5 eV ionization photons. Lower panel: the anisotropy parameter obtained for the CH₂+CO channel.

channel at 157.6 nm is only ~ 8 kcal/mol, which is consistent with the experimentally observed $P(E_T)$. The averaged translational energy release $\langle E_T \rangle$ is only 0.9 kcal/mol, indicating only 11% of the total available energy is deposited to the product translational energy. This suggests that most of the available energy is deposited into the internal energy of the two radicals (CH and HCO). The product angular anisotropy parameter of this channel was determined to be zero, this dissociation channel dissociated through an intermediate that lives much longer than the rotational period of the parent molecule. Clearly, this channel requires a H atom migration before bond dissociation. It is quite possible that the dissociation of this channel occurs via internal conversion to the ground before dissociation occurs, suggesting that dissociation of this channel might be rather statistical. The translational energy distribution $P(E_T)$ for this channel shows a peak at 0.9 kcal/mol, implying that this process has a small dissociation barrier of 0.9 kcal/mol.

C. HCCO+H channel

The H atom elimination channel has also been observed. The TOF signals at different angles have been detected at mass $41(\text{HCCO}^+)$. Two of the spectra are shown in Fig. 6. These TOF spectra can be simulated using the translational energy distribution shown in Fig. 7. The translational energy distribution for the H elimination process peaks at ~ 13 kcal/mol and the sharp cutoff at kinetic energy of



FIG. 5. (a) TOF spectra of mass 29 product at the laboratory angle of 30° using 11 eV photon energy. Curve 1 is the contribution from the ¹³CO simulated by CH₂+CO channel. Curve 2 was simulated by HCO+CH channel. (b) TOF spectra of mass 13 at the laboratory angle of 30° using 12.8 eV photon energy. The solid lines are the simulated contributions from three channels: (1) cracking of the CH₂ radical from CH₂+CO channel, (2) CH product from CH+HCO channel, and (3) cracking of HCCO radical from H elimination channel.

56 kcal/mol, which is a little below the available energy, 66 kcal/mol. About 30% of the total available energy is deposited in the translational degrees of freedom, indicating that majority of the available energy is deposited into the internal energy degrees of freedom of the HCCO radical.

In the ketene photodissociation at 193 nm,²¹ the experimental results suggest that the H atom elimination C-H bond occurs on the S_0 PES. The maximum of the total kineticenergy release (TKER) of the H elimination channel at 193 nm is about 44.3 kcal/mol, and it peaks at \sim 3.8 kcal/mol. For the ketene photodissociation at 157.6 nm, the internal excitation of the hot HCCO radical is clearly higher than that at 193 nm. Anisotropy parameter β was also found to be zero for this channel at 157 nm. It is interesting to point that the peak position of the translational energy distribution for this channel at 157.6 nm, \sim 13 kcal/mol, is much higher than that at 193 nm. This indicates that the dynamics of ketene photodissociation at 157 nm is slightly different from that at 193 nm. If ketene photodissociation at the two wavelengths are similar and occurs on the ground-state surface via internal conversion with energy fully randomized, the peak position of the product translational energy should be more or less the same for the two wavelengths. However, this is not the case here, which



FIG. 6. The TOF spectra of mass 41(HCCO) product at the laboratory angles of 20° and 30° using 12.8 eV photon energy. The open circles are the experimental data points, while the solid lines are the simulated contributions.

suggests that the H atom elimination may not be fully statistically albeit it is possible that this channel occurs on the ground state. This is likely due to the dynamical imprint from the internal conversion that affects the H atom elimination dynamics. No H atom signal has been detected for this channel using the same setup. This is probably due to the low signal levels of these channels, which is likely beyond the sensitivity of our apparatus.



FIG. 7. The translational energy distribution used to simulate the TOF spectra of the dissociation products from the H atom elimination channel. The error bars for the two distribution are about $\pm 10\%$.

TABLE I. Branching ratios for all product channels in photolysis of ketene at 157.6 nm.

Dissociation channel	Branching ratio (%)
CH ₂ +CO	97
CH+HCO	0.9
HCCO+H	2.1

D. Branching ratios

The relative branching ratios of different ketene photodissociation channels at 157.6 nm have been determined. To determine the branching ratios, we have measured all of the TOF signals that could be detected at the ionization photon energy at 17 eV in order to mimic the condition of the electron impact ionization, where the photoionization cross section do not drastically. In the estimation of the branching ratios, we assume that the detection efficiency is the same for all the detected fragments. This assumption of estimating branching ratios has been proved to quite reasonable.²² The estimated branching ratios are listed in Table I.

The dominant channel of ketene photodissociation at 157.6 nm is the CH_2+CO channel. Clearly the dynamics of this dissociation is significantly different from the other two channels. This dissociation process occurs likely via a strong coupling between the excited Rydberg state and a repulsive state, while the other two photodissociation channels, CH +HCO and HCCO+H, proceed likely via internal conversion to the ground state from the excited Rydberg state. The observed branching ratios reflect largely the relative strengths of the two type couplings. Obviously, the excited state couples to the repulsive much more strongly than that to the ground state.

IV. CONCLUSIONS

Photodissociation dynamics of ketene at 157.6 nm has been investigated using photofragment translational spectroscopy (PTS). Three distinct dissociation pathways have been observed. The dominant dissociation channel is CH2+CO with 97% yield, while the CH+HCO and H+HCCO channels are also present but with only $\sim 0.9\%$ and $\sim 2.1\%$ yield. Product translational energy distributions for these two dissociation channels have been determined from simulating the experimental time-of-flight spectra. In addition, the averaged product angular anisotropy parameter for the CH2+CO channel is determined to be 0.6, indicating that this dissociation channel should be a rather fast dissociation process via excited states. This dissociation channel is likely via an intersystem crossing process from the Rydberg excited surface, $3 {}^{1}A_{1}(3d)$, to a direct dissociation state with very strong coupling. The experimental results indicate that both CH +HCO and H+HCCO channels have an anisotropy parameter of zero, implying that these two channels likely occur on the ground surface through internal conversion from the excited surface, even though the dissociation is not necessary fully statistical.

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