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COMMUNICATIONS

Site specificity in molecular hydrogen elimination from photodissociation of propane at 157 nm

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Site effects on the molecular hydrogen elimination from propane at 157 nm excitation have been studied using the photofragment translational spectroscopic technique. Experimental results indicate that H₂ elimination from the internal carbon of propane (2,2-elimination) is predominant while eliminations from the terminal carbon (1,1- and 1,3-elimination) and the vicinal carbons (1,2-elimination) are minor. The translational energy distributions obtained for these processes also show that the dynamics of H₂ eliminations from different sites are significantly different. Relative branching ratios of the atomic hydrogen (H) and the molecular hydrogen (H₂) elimination processes were also determined. © *1999 American Institute of Physics*. [S0021-9606(99)01829-2]

Photodissociation of saturated hydrocarbons (alkanes) is a fundamentally important and interesting subject. It has been established that molecular detachment processes play a significant role in the photolysis of methane (CH_4) ,^{1,2} ethane (CH_3CH_3) ,³ propane $(CH_3CH_2CH_3)$,⁴ and *n*-butane $(CH_3CH_2CH_2CH_3)^5$ under vacuum ultraviolet (VUV) light excitation. However, molecular hydrogen elimination processes from saturated hydrocarbons have rarely been studied systematically using modern experimental techniques. This is partly due to the lack of access of high power pulsed lasers in the VUV region where saturated hydrocarbon molecules start to absorb.

Dynamics of the atomic hydrogen elimination processes from the photodissociation of CH_3CH_3 and $CH_3CH_2CH_3$ at Lyman- α (121.6 nm) excitation have been recently studied using the velocity map imaging technique,⁶ and CH_4 has been extensively investigated in detail with its isotopomers in the past few years.^{2,7-9} Chandler and co-workers have also measured the $H_2(v,J)$ photofragment images following the two-photon absorption which deposits 10.8–11.8 eV of energy in a methane molecule.² They observed that there are two molecular hydrogen elimination channels, which are the direct two-body dissociation process ($CH_4 \rightarrow CH_2 + H_2$) and the three-body dissociation process ($CH_4 \rightarrow CH + H_2 + H$). Propane is the smallest saturated hydrocarbon that has sufficient absorption at 157 nm excitation.^{10–12} The site specificity of the atomic elimination process from the photodissociation of propane at 157 nm excitation has been investigated using the Doppler spectroscopic technique by Tonokura *et al.*¹³ Their experimental results showed that the hydrogen atom products mostly come from the terminal carbons of propane. The energy diagram of possible products from the photodissociation of propane at 157 nm excitation is shown in Fig. 1. At the excitation of this high photon energy (181.4 kcal/mol or 7.87 eV), methyl radical (CH₃), methane molecule (CH₄), atomic hydrogen (H), and molecular hydrogen (H₂) elimination processes, and many different triple dissociation pathways are energetically accessible. The molecular hydrogen could be eliminated via the following pathways:

$$CH_3CH_2CH_3 + h\nu(157 \text{ nm}) \rightarrow CH_3CH_2CH + H_2$$
(1)

 \rightarrow CH₃CCH₃+H₂ (2)

$$\rightarrow$$
 CH₃CH=CH₂+H₂ (3)

$$\rightarrow CH_2CH_2CH_2+H_2$$
 (4)

$$\rightarrow CH_3C \equiv CH + 2H_2$$
 (5)

$$\rightarrow$$
 CH₂=C=CH₂+2H₂ (6)

$$\rightarrow C_3H_5 + H_2 + H. \tag{7}$$

The first channel is the molecular hydrogen elimination from the terminal carbon of propane (1,1-elimination), the second channel is from the internal carbon (2,2-elimination), the third channel is from the vicinal carbons (1,2-elimination), and the fourth channel is from the two terminal methyl

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FIG. 1. Energy diagram of some possible product channels from the photodissociation of propane at 157 nm (7.87 eV) excitation. The relative energies were calculated from the heat of formation of the species (see Ref. 21).

groups (1,3-elimination). The final three channels are the triple dissociation processes. As we can see from the above, H_2 products may come from many possible combinations of different sites.

The absorption spectra of the alkanes from propane to n-octane in the VUV region are continuous with no clear vibrational structure.^{10,14} There is weak absorption between 163.0 and 157.5 nm in all the spectra from ethane to *n*-octane. However, no clear consensus has been reached yet on the assignment of these absorption bands. Raymonda and Simpson assigned those to an intramolecular charge transfer excitation between adjacent C–C bonds,¹¹ while Robin assigned as a Rydberg excitation to 3s,¹² and Sandorfy and co-workers suggested the excitation is localized mainly in one ethyl group.¹⁰ Theoretical calculations^{15,16} shows that the vertical transition energy to the 3s Rydberg orbital is about 1 eV higher than the starting absorption energy of the first absorption shoulder. This, however, is not necessarily contradictory to the assignment of the lowest absorption of propane to the 3s Rydberg absorption since vertical transition energy could be much higher than the adiabatic transition energy due to large geometric changes between the initial and final electronic states.¹⁷ In any case, the identity of the first absorption shoulder needs to be further clarified.

A photofragment translational spectroscopic technique was used to study the photodissociation of propane in this work. The main thrust of this study is to understand the molecular hydrogen elimination processes from propane. The apparatus used in this work has been previously described.¹⁸ Briefly, it contains two source chambers, a main chamber and a rotatable detector. The most crucial part for

this study is the ultraclean detector in the apparatus. The ultrahigh vacuum $(1 \times 10^{-12} \text{ Torr})$ in the electron impact ionization region reduces the H₂ background by almost 2 orders of magnitude in comparison to other similar apparatus. Thus, the detection of the molecular and atomic hydrogen channels becomes much easier. An unpolarized 157 nm laser beam (Lambda Physik LPX 210*i*, F₂ laser) with about 1 mJ/pulse laser power was focused to a spot size of \sim 4 mm \times 4 mm in the interaction region. The laser beam was crossed with the propane molecular beam perpendicularly in at a distance of ~ 8 mm away from the nozzle tip. A 50 Hz pulsed propane beam was produced by expanding the neat propane sample from a solenoid valve (General Valve) through a 0.5-mm-diam orifice at the backing pressure of about 80 Torr. The flight distance of the neutral products was 285 mm and the detection axis was orthogonal to both the laser beam and the molecular beam. All experimental conditions such as molecular number density, and laser intensity in the interaction region were well controlled in order to make meaningful comparisons. Multiphoton effect and molecular clustering effect were carefully checked and avoided.

Time-of-flight (TOF) spectra of the photodissociation products at m/e = 1,2 from CH₃CH₂CH₃ and at m/e= 1,2,3,4 from $CH_3CD_2CH_3$ at 157 nm excitation are shown in Fig. 2. The experimental study on CH₃CD₂CH₃ aims to clarify the sources of molecular hydrogen elimination processes. In order to know the exact relative contributions of different products, detection efficiencies of H_2 , HD, and D_2 were calibrated by measuring the signal intensities of the continuous effusive beam consisting of an equimolar mixture of H₂, HD, and D₂ at m/e = 2, 3, and 4. Since total ionization cross sections of H₂ and D₂ are known to be nearly identical,¹⁹ HD is expected to have the same ionization cross section as H_2 and D_2 . From the relative detection of H_2 , HD, D₂, detection efficiency of the H atom at m/e = 1 could be estimated since the ratio of the ionization efficiency of atomic and molecular hydrogen was known.¹⁹ Since dissociative ionization of molecular hydrogen by the electron bombardment at ~ 60 eV electron energy is negligible,¹⁹ the TOF spectra at m/e = 1 and 2 shown in Fig. 2(a) should be the photofragment signals of H and H₂, respectively. The TOF spectra at m/e = 1, 2, 3, and 4 shown in Fig. 2(b) are the photofragment signals of H, D and H₂, HD, and D₂, respectively. The D/H ratio from the photodissociation of $CH_3CD_2CH_3$ at 157 nm has been reported to be ~0.07:1 by comparing the total areas under the Doppler profile.¹³ Since the signals at m/e = 1 come only from the H atom in this experiment, the D atom contributions to m/e=2 should be very small by comparing the signals and the D/H ratio. H atom Rydberg tagging experiment in our laboratory also confirms this result. Thus, the signals at m/e=2 shown in Fig. 2(b) should mostly come from the photodissociation products of H₂. The solid curves shown in Fig. 2 are the simulated TOF spectra using the translational energy distributions, shown in Fig. 3, for atomic and molecular hydrogen elimination channels from the photodissociation of CH₃CH₂CH₃ and CH₃CD₂CH₃. The simulations were carried out using a recently developed software package, CMLAB3, which is modified from the previous version, CMLAB2.²⁰ All



FIG. 2. TOF spectra of the photodissociation products from (a) $CH_3CH_2CH_3$ and (b) $CH_3CD_2CH_3$. The spectra were accumulated over 100 k laser shots, and calibrated by the detection efficiencies of different species. The open shapes corresponding to curve 1, 2, 3, and 4 are the experimental results at m/e = 1, 2, 3, and 4, respectively. Curve 1, 2 in (a), and curve 1, 2, 3, 4 in (b) are the simulated TOF calculated from the translational energy distributions which are curves a1, a2, b1, b2, b3, and b4 shown in Fig. 3, respectively.

the translational energy distributions were obtained assuming that the dissociation products were from a binary dissociation process.

As shown in Fig. 3, curve a1 is the translational energy distribution of the H atom elimination and curve a2 is that of the H_2 elimination from the photodissociation of CH₃CH₂CH₃. From Fig. 2(a), H₂ elimination from propane is clearly the dominant process, while H elimination is minor. The H₂/H branching ratio was determined to be 2.1 by calculating the integral ratio of the two channels in the center-of-mass frame. The translational energy distributions for the H and H₂ elimination processes are significantly different. The translational energy distribution for the H_2 elimination process (curve a2) has two peaks. The lower energy peak is at ~ 30 kcal/mol and the higher one is at ~ 61 kcal/mol, indicating there are at least two different dynamical processes involved in the H₂ elimination from normal propane. The translational energy distribution of the H elimination process (curve a1) peaks at 0 kcal/mol.

Curve b1 in Fig. 3 is the translational energy distribution for the H elimination from the photodissociation of $CH_3CD_2CH_3$. Similar to the case of $CH_3CH_2CH_3$, the translational energy distribution also peaks at 0 kcal/mol. The



FIG. 3. Translational energy distributions used to fit the TOF spectra of the products of the atomic and molecular hydrogen elimination channels from the photodissociation of $CH_3CH_2CH_3$ and $CH_3CD_2CH_3$. Curves a1 and a2 are, respectively, the translational energy distributions of the H and H₂ elimination channels from $CH_3CH_2CH_3$. Curves b1, b2, b3, and b4 are, respectively, the translational energy distributions of the H, H₂, HD, and D₂ elimination channels from $CH_3CD_2CH_3$. The relative heights of the distributions are arbitrary.

energy release of the H atom elimination is also very small, indicating that the H atom process likely proceeds via a secondary dissociation process without an exit barrier. There are some small, but obvious, differences between the two translational energy distributions for the H atom elimination processes from CH₃CD₂CH₃ and CH₃CH₂CH₃. At higher energies, the translational energy distribution for the H elimination from CH₃CH₂CH₃ is quite larger than from CH₃CD₂CH₃. This may mainly be due to the H detachment from the internal carbon. The argument is also supported from the preliminary results of the photodissociation of CD₃CH₂CD₃. Curve b2 is the translational energy distribution obtained for the H_2 elimination (1,1- and 1,3elimination) from the photodissociation of CH₃CD₂CH₃ and peaks roughly around 20-30 kcal/mol. It is immediately clear that the translational energy distribution (b2) from $CH_3CD_2CH_3$ is significantly different from that (a2) for the H₂ elimination from CH₃CH₂CH₃. Curve b3 in Fig. 3 is the translational energy distribution of the HD elimination (1,2elimination) and peaks at \sim 61 kcal/mol, and curve b4 in Fig. 3 is the translational energy distribution of the D_2 elimination (2,2-elimination) and peaks at \sim 31 kcal/mol. The translational energy distribution (b3) for the HD elimination process from CH₃CD₂CH₃ is also significantly different from that for the H₂ elimination from CH₃CH₂CH₃, while the translational energy distribution (b4) for the D_2 elimination from CH₃CD₂CH₃ is quite similar to that for the H₂ elimination from CH₃CH₂CH₃. The relative branching ratios of the molecular hydrogen elimination processes from CH₃CD₂CH₃ are listed in Table I. The ratio for the overall molecular hydrogen (H₂, HD, and D₂) to the H elimination channel from $CH_3CD_2CH_3$ is determined to be 2.2, which is quite close to the H_2/H branching ratio for the normal propane (2.1). From the relative branching ratios (Table I) of the three molecular elimination channels, it is clear that the 2,2-elimination from the photodissociation of $CH_3CD_2CH_3$ is predominant (75%), i.e., the molecular hydrogen products mostly come from the central carbon. Other types of H₂ elimination are minor. In

TABLE I. Relative yields of molecular hydrogen elimination channels from the photodissociation of $CH_3CH_2CH_3$ and $CH_3CD_2CH_3$.

Molecule	1,1-E and 1,3-E	1,2-Е	2,2-Е
CH ₃ CH ₂ CH ₃	9 ^a	14 ^a	77 ^a
CH ₃ CD ₂ CH ₃	6	19	75

^aThe relative yields come from the fitting ratios for curves 1, 2, and 3 shown in Fig. 4.

the H_2 elimination from the terminal CH₃ groups, there are two possible types of elimination processes: 1,1-elimination and 1,3-elimination. In this experiment, we are not able to differentiate the two pathways. A closer look at these dissociation pathways is under way in our laboratory. The site specificity observed for the molecular elimination here is very interesting since it is exactly the opposite of the atomic hydrogen elimination in which the dominant process is the H elimination from the terminal CH₃ groups. It is also interesting to notice that the dynamics for all these processes are significantly different from each other, indicating that no isotope scrambling occurs in the dissociation process of propane.

Since total H₂ elimination from CH₃CH₂CH₃ is the combination of different site H₂ elimination processes: 1,1- and 1,3-elimination, 1,2-elimination, and 2,2-elimination, the experimental TOF spectrum at $m/e = 2(H_2)$ from CH₃CH₂CH₃ can be fitted using the translational energy distributions of these different processes obtained from the photodissociation of CH₃CD₂CH₃. Figure 4 shows the experimental and simulated TOF spectra of the H₂ product. The agreement between experiment and simulation is quite good. The relative branching ratios obtained for different H₂ elimination processes from the photodissociation of CH₃CH₂CH₃ are listed in Table I. The results are very similar to those obtained for the photodissociation of CH₃CD₂CH₃, indicating that the



FIG. 4. Site-specific TOF spectrum of the H_2 elimination channel from the photodissociation of $CH_3CH_2CH_3$. The open circles are the experimental data, while the solid lines are the fits to the spectrum using the translational energy distributions of the molecular hydrogen elimination processes from $CH_3CD_2CH_3$ shown in Fig. 3. Curves 1, 2, and 3 are fitted from the H_2 , HD, and D_2 elimination processes, respectively; curve 4 is the overall fit.

picture provided above for the molecular hydrogen elimination should be correct. Therefore it is clear that the isotope effects are not significant. From Fig. 4, all translational energy distributions for molecular hydrogen elimination processes extend to higher energy limit, indicating that molecular hydrogen elimination processes are likely primary dissociation processes. And from the relative branching ratios, it is apparent that molecular H_2 elimination processes from propane are very nonstatistical, while the H atom elimination is likely a statistical process.

From the above experimental investigations, a very clear picture of the atomic and molecular hydrogen elimination processes is presented. Molecular hydrogen elimination from the photodissociation of propane at 157 nm excitation is found to be significantly more important than the atomic hydrogen elimination process. Molecular hydrogen elimination mostly proceeds via direct two-body dissociation pathways, and is primarily from the internal carbon (2,2-elimination). The dynamics of different molecular hydrogen elimination processes from different sites are also significantly different.

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