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Site and isotope effects on the molecular hydrogen elimination from ethylene at 157 nm excitation

Jim J. Lin and Dennis W. Hwang
Department of Chemistry, National Taiwan University, Taiwan, Republic of China

Yuan T. Lee
Department of Chemistry, National Taiwan University and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic of China

Xueming Yang[a)]
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic of China

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Site and isotope effects on the molecular hydrogen elimination from ethylene have been studied from the photodissociation of ethylene at 157 nm excitation. Experimental results show that there are three different types of molecular elimination processes: 1,1 elimination, 1,2-*cis* elimination, and 1,2-*trans* elimination. These elimination processes show significantly different translational energy distributions. Isotope effect on the dynamics of these molecular hydrogen elimination processes has been also investigated carefully. © *1998 American Institute of Physics.* [S0021-9606(98)01332-4]

Molecular elimination from highly excited molecules is an important and also interesting class of unimolecular reactions since it is related not only to simple bond rupture processes but also bond formation processes during the elimination. However, there has been lack of systematic studies on the dynamics of the molecular hydrogen elimination so far, especially the precise translational and internal energy distributions of the photodissociation products. Recently, a new universal crossed beam apparatus has been established in our laboratory.[1] Because of its extremely low background of H_2 in the detector, this new apparatus provides us a unique and excellent tool to study the interesting molecular hydrogen elimination process.

Previous experimental studies[2–7] show that the dissociation of ethylene under the excitation of a high energy photon involves four different chemical dissociation channels,

$$C_2H_4 + h\nu \rightarrow HC{\equiv}CH + H_2 \quad (1)$$

$$\rightarrow H_2C{=}C{:} + H_2 \quad (2)$$

$$\rightarrow H_2C{=}CH + H \quad (3)$$

$$\rightarrow HC{\equiv}CH + 2H. \quad (4)$$

The first two channels are the molecular hydrogen elimination processes, while the third and the fourth channels are the atomic hydrogen elimination processes. Molecular hydrogen elimination has been studied in the photodissociation of ethylene at 193 nm excitation.[8–10] Site and isotope effects on the dynamics of molecular hydrogen elimination from ethylene have been investigated qualitatively.

The molecular elimination process in ethylene can be divided into three types of elimination: 1,1 elimination ($11E$), 1,2 *cis* elimination ($12cE$) and 1,2 *trans* elimination ($12tE$). In each of the three types of elimination, there are two possible pairs of hydrogen atoms for molecular elimination (see Fig. 2). In this work, photodissociation of different ethylene isotopomers at 157 nm excitation are systematically investigated in order to examine the site and isotope effects on the dynamics of molecular hydrogen elimination from ethylene. At 157 nm excitation, the ethylene molecule is mainly excited to the $3p_{x,y,z}$ Rydberg states.[11] The equilibrium geometries of the $3p_{x,y,z}$ Rydberg states are all near planar from a recent theoretical calculation,[12] implying that the 1,2 *cis* and *trans* molecular eliminations can be dynamically different.

The apparatus used in this experiment is a newly built universal crossed beam machine. A detailed description of this apparatus can be found somewhere else.[1] Briefly, the new crossed molecular beam apparatus consists of a source chamber, a main chamber and a rotating detector. The most crucial part of the apparatus is its ultraclean UHV universal detector. The ionization detection region can be maintained to a vacuum of 1×10^{-12} Torr or lower in the new apparatus. The H_2 background in the detector is about 2 orders of magnitude lower in comparison with any similar apparatus. This made the detection of molecular hydrogen, therefore atomic hydrogen, much easier than before. The 157 nm photolysis laser beam from a Lambda Physik LPX 210*i* laser is focused into the ethylene molecular beam at a distance of 10 mm away from the nozzle. In a typical experiment, a 50 Hz pulsed ethylene beam is produced by expanding the neat ethylene from a pulsed valve (General Valve) through a 1 mm diam nozzle at a pressure of 50 Torr behind the nozzle. In this work, the dynamics of the photodissociation of three di-deuterated ethylene isotopomers: 1,1-CH_2CD_2, 1,2 *cis*-CHDCHD, and 1,2 *trans*-CHDCHD are investigated. In order to make meaningful comparisons across the three ethylene isotopomers, all experimental conditions such as molecular number density, and laser intensity in the interaction area are controlled carefully.

Time of flight spectra of the photodissociation products at $m/e=1,2,3,4$ from the ethylene isotopomers at 157 nm

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[a)] Author to whom correspondence should be addressed. Electronic mail: xmyang@po.iams.sinica.edu.tw

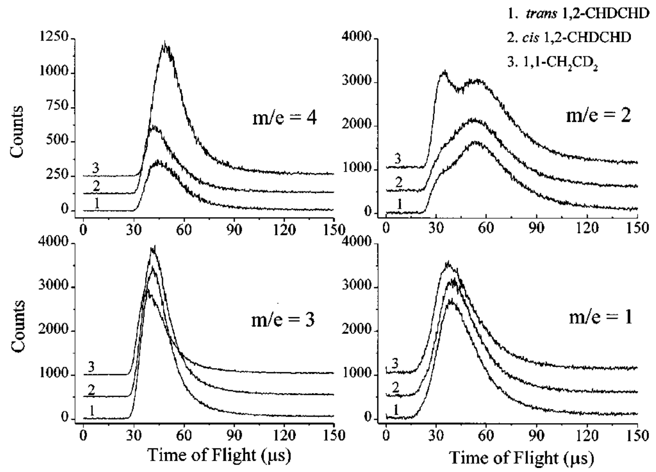

FIG. 1. TOF spectra for photodissociation products at $m/e=1,2,3,4$ from the three ethylene isotopomers. All spectra were taken by averaging over 25 000 laser shots.

excitation were recorded at the perpendicular direction of the molecular beam using the experimental method described above. Figure 1 shows the time of flight spectra of $m/e=1,2,3,4$ from the photodissociation of the three dideuterated ethylene isotopomers. In order to know if a meaningful comparison can be made across all isotopomers, the total photodissociation signals (from $m/e=1$ to 4) from the three ethylene isotopomers were compared. Without considering the transformation (lab to center-of-mass frame) differences between different isotopomers, which are considered to be small since the shape of the total signal of the three compounds are quite similar, the integrated signals from the three di-deuterated ethylenes were all within 5% to each other, indicating that the photodissociation of three deuterated ethylene molecules can be compared quantitatively. It is necessary to point out that the anisotropy differences in the dissociation processes might also cause some differences in the branching ratio. However, experimental results here show that molecular hydrogen elimination from ethylene most likely occurs on the ground potential surface through internal conversion from the initially excited state. This will probably wash out most of the anisotropy in the dissociation processes.

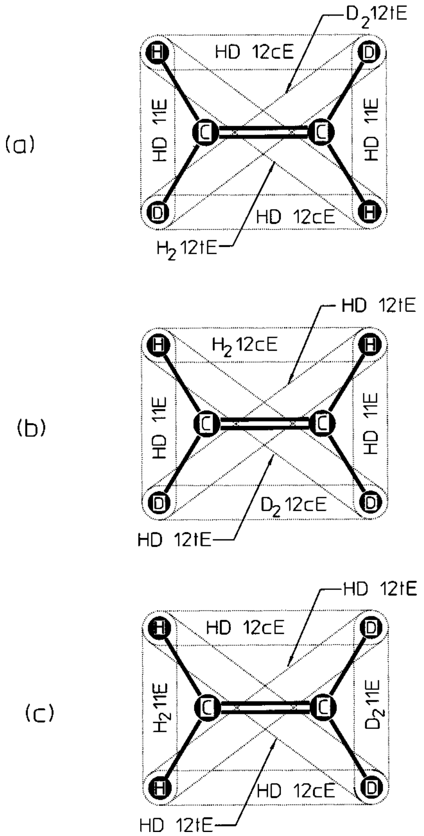

FIG. 2. Molecular elimination channels from the three ethylene isotopomers. (a) 1,2 *trans*-CHDCHD; (b) 1,2 *cis*-CHDCHD; (c) 1,1-CH_2CD_2.

TABLE I. Relative yields of H_2, HD, and D_2 eliminations from the three ethylene isotopomers.

Molecule	D_2	HD	H_2	Total
1,2 *trans*-CHDCHD	1.00	8.58	1.90	11.48
1,2 *cis*-CHDCHD	1.30	8.18	1.90	11.38
1,1 CH_2CD_2	2.29	5.20	4.12	11.61

Since the dissociative ionization of the hydrogen molecule can be neglected, the observed signals at $m/e=1,2,3,4$ should be the photodissociation products of H, H_2 and D, HD and D_2, respectively. Therefore from the experimentally measured time of flight spectra for $m/e=1,2,3,4$, the translational energy distribution of different elimination channels, atomic and molecular eliminations, can be obtained using a previously developed software package, CMLAB2.[12] The detection efficiencies for the H_2, HD, and D_2 products are all assumed to be the same in the analysis. By fitting the time of flight spectra of $m/e=2,3,4$ from all three isotopomers, the translational energy distributions and yields for each channel have been derived. Figure 3 shows the experimental data and simulated fits to the time-of-flight spectra of the D_2 products from the photodissociation of the three isotopomers using the translational energy distributions shown in Fig. 4(a). It is clear, from Fig. 2, that the H_2 and D_2 eliminations from all three deuterated ethylenes are site-specific. The H_2 and D_2 eliminations from 1,2 *trans*-CHDCHD are all due to site specific 1,2 *trans* elimination ($12tE$), the H_2 and D_2 eliminations from 1,2 *cis*-CHDCHD are all due to site specific 1,2 *cis* elimination ($12cE$), and the H_2 and D_2 eliminations from 1,1-CH_2CD_2 are all due to site specific 1,1 elimination ($11E$). While H_2 and D_2 eliminations are all site specific, the HD eliminations from the three deuterated compounds are the combination of two different site eliminations (see Fig. 2). As shown in Fig. 2, the HD elimination from 1,2 *trans*-CHDCHD is the combination of the 1,1 HD elimination and the 1,2 *cis* HD elimination; the HD elimination from 1,2 *cis*-CHDCHD is the combination of the 1,1 HD elimination and the 1,2 *trans* HD elimination; and the HD elimination from 1,1-CH_2CD_2 is the combina-

TABLE II. Relative yields of specific site H_2, HD, and D_2 eliminations.

Specific site elimination	D_2	HD	H_2
1,2 *trans* elimination (12tE)	1.00	1.20	1.90
1,2 *cis* elimination (12cE)	1.30	1.40	1.90
1,1 elimination (11E)	2.29	2.89	4.12

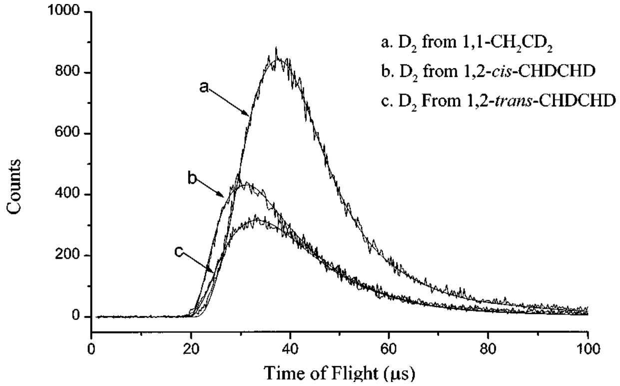

FIG. 3. Experimental and simulated TOF spectra of the D_2 products from photodissociation of the three isotopomers. The translational energy distributions used in the simulation are shown in Fig. 4(a).

tion of the 1,2 *cis* HD elimination and the 1,2 *trans* HD elimination.

From the simulation of the time of flight spectra, the relative yields of the H_2, HD, and D_2 eliminations from the three isotopomers can be obtained, which are all listed in Table I. Since the H_2 and D_2 elimination processes are site specific, the relative yields listed for the H_2 and D_2 eliminations in Table I are also site specific. The HD elimination from each ethylene isotopomer, however, is a combination of two specific site eliminations as pointed above. Therefore the total HD yields listed in Table I are not site specific. In order to determine the site specific HD yield, the total HD yield from each deuterated ethylene can be viewed as the summation of the two site specific HD yields, and each specific site HD yield from different deuterated ethylene molecules is assumed to be the same,

$$Y_{\mathrm{HD}}(1{,}2\ \textit{trans}\text{-CHDCHD})=2y_{\mathrm{HD}}(11E)+2y_{\mathrm{HD}}(12cE), \tag{5}$$

$$Y_{\mathrm{HD}}(1{,}2\ \textit{cis}\text{-CHDCHD})=2y_{\mathrm{HD}}(11E)+2y_{\mathrm{HD}}(12tE), \tag{6}$$

$$Y_{\mathrm{HD}}(1{,}1\text{-CH}_2\text{CD}_2)=2y_{\mathrm{HD}}(12cE)+2y_{\mathrm{HD}}(12tE), \tag{7}$$

where Y_{HD} is the total yield of HD elimination, and y_{HD} is the yield of site specific HD elimination. Solving the above equations, the relative yields for the site specific HD eliminations can be obtained. Table II lists the relative yields of the H_2, HD, and D_2 site specific eliminations.

The translational energy distributions for the site specific eliminations of H_2, HD, and D_2 are also obtained through the simulation using the CMLAB2 program. Since the H_2 and D_2 eliminations are all site specific, the translational energy distributions obtained for these processes are all site specific. However, the translational energy distributions for site specific HD eliminations from the three deuterated compounds can be obtained using a similar method to the calculations of the site specific HD yields. Here, the translational energy distribution of the HD elimination from a di-deuterated ethylene can be viewed as the summation of the contributions of the two site specific HD eliminations,

$$P_{12t}(E)=2p_{11E}(E)+2p_{12cE}(E), \tag{8}$$

$$P_{12c}(E)=2p_{11E}(E)+2p_{12tE}(E), \tag{9}$$

$$P_{11}(E)=2p_{12tE}(E)+2p_{12cE}(E), \tag{10}$$

where $P_{12t}(E)$, $P_{12c}(E)$, and $P_{11}(E)$ are the translational energy distribution for the total HD elimination from 1,2 *trans*-CHDCHD, 1,2 *cis*-CHDCHD, 1,1-CH_2CD_2 respectively, while $p_{12tE}(E)$, $p_{12cE}(E)$, and $p_{11E}(E)$ are the translational distribution for each specific site HD elimination: 1,2 *trans* elimination, 1,2 *cis* elimination and 1,1 elimination, respectively. From the measured translational distributions $P_{12t}(E)$, $P_{12c}(E)$, and $P_{11}(E)$, the translational energy distributions $p_{12tE}(E)$, $p_{12cE}(E)$, and $p_{11E}(E)$ for the site specific HD elimination can be determined by solving the above equations. Up until now, all translational energy distributions for different sites and isotopes have been determined. The

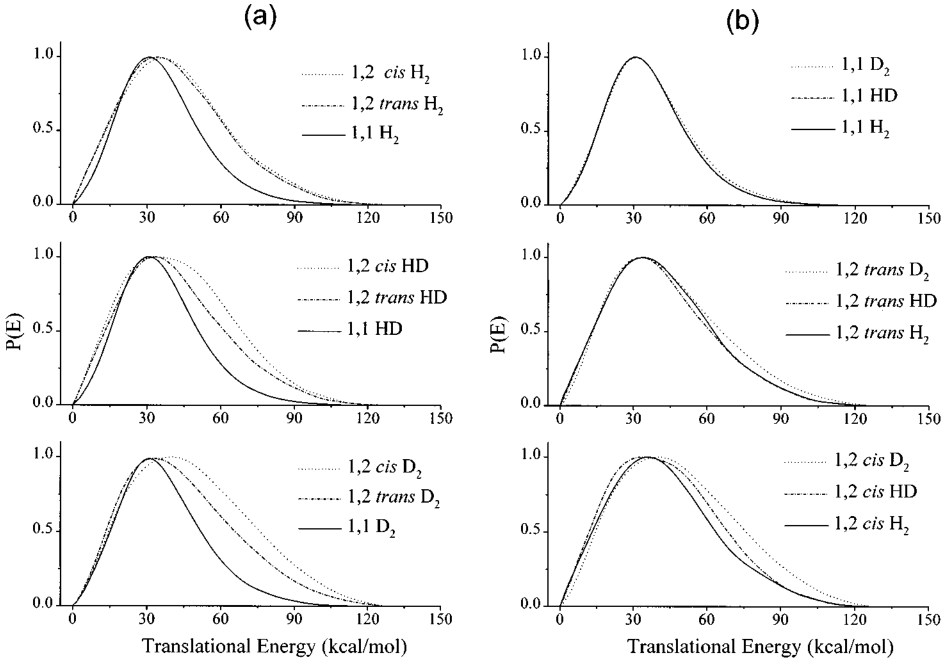

FIG. 4. (a) Site effect on the $P(E)$'s for D_2, HD, and H_2 elimination; (b) Isotope effect on the $P(E)$'s for specific site elimination.

specific site effect on the translational energy distribution of the H_2, HD, and D_2 elimination is shown in Fig. 4(a), while the isotope effect on the translational energy distribution of specific site eliminations is shown in Fig. 4(b). For convenience of comparison, all translational energy distributions shown in Figs. 3(a) and 3(b) are normalized to the same height.

From the translational energy distributions and yields for the specific site H_2, HD, and D_2 elimination [see Fig. 4(a) and Table II], it is very clear that the 1,1, 1,2 *cis* and 1,2 *trans* D_2 elimination processes show significant differences in their kinetic energy distributions, indicating that the dynamics of D_2 elimination from different sites are quite different. The difference between the 1,2 *cis* and 1,2 *trans* D_2 elimination is especially interesting because all previous studies at different wavelength excitations show no differences between these two microchannels. The HD eliminations from different sites also show significant differences in their translational energy distributions. For the H_2 elimination processes, however, the differences between the 1,2 *cis* and *trans* H_2 eliminations have diminished. It is clear that the four center molecular elimination requires a 1,2 hydrogen atom migration. The transition state of the 1,2 elimination is believed to be the so-called ethylidene radical $(:CHCH_3)$.[13–17] Recent theoretical studies on the ethylene photodissociation show that the structures of the transition state of the 1,2 *trans* and the 1,2 *cis* elimination processes are slightly different.[17] This will certainly cause some differences between the dynamics of the 1,2 *cis* and *trans* elimination processes. The main difference shown in the dynamics of 1,2 *cis* and *trans* eliminations cannot, however, be solely explained by the differences in the transition states.[17] Other dynamical processes such as 1,2 concerted molecular hydrogen elimination, which does not require 1,2 hydrogen atom shift, might be responsible for the main difference between the *cis* and *trans* molecular hydrogen eliminations. It is certainly conceivable that the concerted molecular hydrogen eliminations from *cis* and *trans* configurations might be quite different because the distances between the two hydrogen atoms are significantly different in the two type eliminations in which tunneling effects might be important.

The isotope effect on the translational energy distribution is also quite interesting. For the three center elimination channel (1,1 molecular hydrogen elimination), the translational energy distributions for H_2, HD, D_2 are almost exactly the same [see Fig. 4(b)] implying that the isotope effect on the dynamics of the 1,1 elimination channel are very small. The isotope effect on the translational energy distributions for the four center elimination channels, especially the 1,2 *cis* elimination, is much more significant. From Table II, it is easy to see that the relative yields for any specific site elimination increase as the eliminated species (D_2, HD, and H_2) gets lighter.

From this study, complete and important information on the site and isotope effects on the molecular hydrogen elimination processes from ethylene has been derived. Using the new improved experimental technique, dynamical differences between different microchannels of molecular hydrogen elimination processes from ethylene can be detected. The results of this work provide an excellent test ground for further theoretical investigations of molecular elimination processes of ethylene.

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