Control and Characterization of a Multistep Unimolecular Reaction

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Electrons from a scanning tunneling microscope were used to break a C-H bond in a single acetylene (HCCH) molecule adsorbed on Cu(001) at 9 K. The product ethynyl (CCH) was characterized by imaging, inelastic electron tunneling spectroscopy, and variable temperature measurements of the rotation rate. Significant changes in the vibrational spectra and bonding geometry accompanied HCCH dissociation. The ethynyl was further dehydrogenated to form dicarbon (CC). Dissociation studies of the isotopes HCCD and DCCD permitted unambiguous identification of the reaction products.

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The scanning tunneling microscope (STM) may be applied not only to the observation but also to the chemical transformation of matter on the atomic scale [1]. This avenue of research is of obvious fundamental and practical interest. On the practical side, useful devices of molecular dimensions may be fabricated from individual atoms and molecules as control of chemistry on the atomic scale is developed. On the fundamental side, one can address outstanding questions in surface science in their simplest form by initiating the chemical transformation of individual molecules. Studies of STM induced dissociation have contributed to this area of research [2–6]. The dissociation of decaborane on Si(111) resulted in the creation of several unidentified molecular fragments [2]. The dissociation of Cu-tetra-3,5 di-tertiary-butyl-phenyl porphyrin on Cu(001) consistently resulted in a single reaction product whose complexity precluded definitive identification [3]. Inelastic electron tunneling spectroscopy (STM-IETS) [7] was used to identify acetylene as the dissociation product of ethylene on Ni(110); dissociation of acetylene led directly to atomic carbon [4]. Studies of O_2 dissociation on Si(111) [5] and Pt(111) [6] provided an understanding of different excitation mechanisms.

In this paper, we demonstrate single bond scission in a polyatomic molecule while leaving another identical bond intact: single hydrogen atoms were sequentially removed from acetylene (HCCH) to produce molecular ethynyl (CCH) and dicarbon (CC). STM-IETS was performed to identify the chemical species and characterize the substantial changes in bonding that occurred upon C-H bond scission. The interaction between CCH and the Cu(001) surface was futher explored by measuring thermal rotation rates to extract the energetic barrier to rotation. These results are of interest for several reasons. First, the controlled dissociation method may be applied to selective bond dissociation in larger molecules. Second, the use of STM-IETS in conjunction with controlled dissociation demonstrates the unambiguous identification of reactant, intermediate, and end product in this model, unimolecular dehydrogenation reaction. Acetylene and ethynyl are important in a number of diverse chemical processes including high temperature combustion [8] and reactions catalyzed by metal surfaces [9]. Finally, the breadth of the experimental characterization of ethynyl, including imaging, rotational barriers, vibrational spectra, and dissociation thresholds, provides insight into the physical connections between the measured quantities and will motivate theoretical calculations of both ground and excited state properties of the molecule-surface system.

Experiments were performed using a homebuilt variable temperature STM housed in an ultrahigh vacuum chamber with a base pressure of 2×10^{-11} Torr [10]. The preparation of the Cu(001) sample and tungsten tips has been described previously [11]. Molecules were dosed from gaseous sources to coverages of $\sim$0.001 ML via a capillary array doser attached to a variable leak valve. The surface was held at 9 K unless otherwise indicated.

On the Cu(001) surface, acetylene images as an elongated depression and is found in two equivalent orientations [Figs. 1(a) and 1(b)]. The predominant molecule-surface interaction is di-σ bonding of the two carbon atoms to two copper atoms across the diagonal of the fourfold hollow site [7]. The C-H bonds bend away from the surface and the molecular plane is perpendicular to the surface.

Low energy electrons from the STM tip were used to induce the dissociation of HCCH(DCCD) into CCH(CCD) and CC in a controlled manner. The method will be described below. The CCD species is found in one of four orientations shown in Figs. 1(c)–1(f). The CC species is found in one of two orientations shown in Figs. 1(g) and 1(h). Individual carbon atoms were not resolved. As is generally true of STM images, the size of molecule-related features reflects not simply the size of the molecule but also the perturbation of the native Cu(001) electronic structure. For example, the (red) protrusions in Figs. 1(c)–1(f) are due to the positive contribution of the D atom to the local density of states but do not correspond to the actual location of the D atom.

The controlled dissociation of acetylene was accomplished by placing the tip directly over the molecule to be dissociated, retracting the tip $\sim$3 Å, and raising the sample

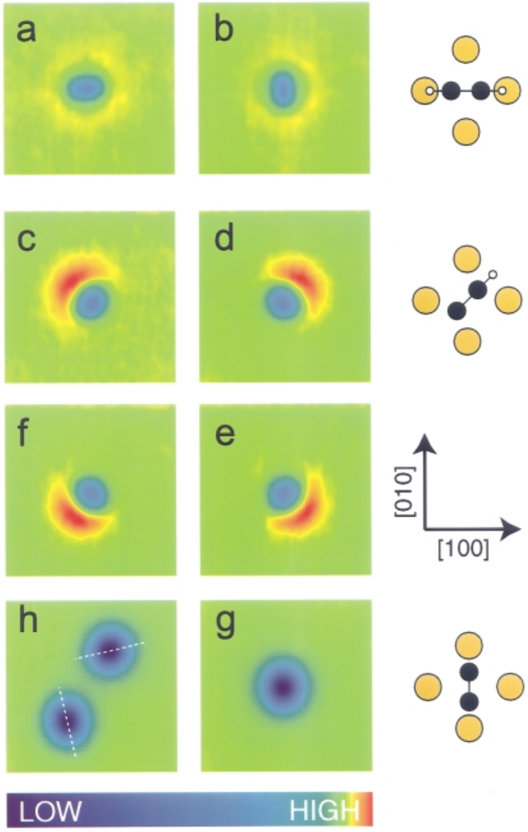

FIG. 1 (color). 38 × 38 Å^2 constant current STM images of DCCD, CCD, and CC. The vertical range is -1.20 to 0.07 Å. All possible orientations of these molecules on the fourfold hollow site are shown. Site assignments were confirmed by simultaneously resolving both the molecules and the copper lattice using a tip modified with an adsorbed species and different tunneling parameters than used for these images. Images of CCH and CCD are nearly identical; CCD is shown because the tip induced rotation rate of CCH is higher, making imaging difficult. (a),(b) DCCD. (c)–(f) CCD. The image minima are displaced 0.7 Å from the fourfold hollow site along the ⟨110⟩ axes. (g),(h) One and two CC molecules, respectively. Images (a)–(g) were taken at 10 pA tunneling current and 50 mV sample bias. Image (h) was taken during a separate experiment at 10 nA and 100 mV to emphasize the difference in molecular orientation. The directions of the Cu[100] and Cu[010] axes are indicated by the dashed white lines and are rotated 20° with respect to those of the other images. Schematics of the molecular orientation are shown next to the images they represent for (b), (d), and (g). The scale is enlarged 5× with respect to the images.

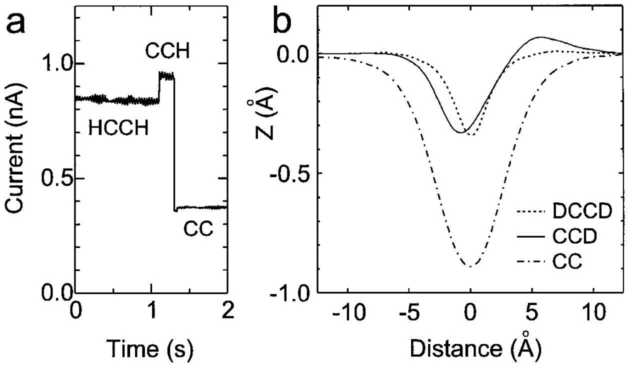

FIG. 2. Salient features of controlled HCCH dissociation. (a) Tunneling current at 3.0 V sample bias with the tip held fixed above the center of an HCCH molecule. The current changes stepwise as the energetic electrons induce C-H bond dissociation. The correspondence between chemical species and current levels is indicated. The bias voltage can be lowered after sensing a positive current step to preserve the CCH species. (b) Constant current contours of DCCD, CCD, and CC were taken from Figs. 1(b), 1(d), and 1(g) along [100], [110], and [010], respectively.

bias to the dissociation voltage. Figure 2(a) shows a typical dissociation sequence in which HCCH is converted into CCH and CC sequentially by 3.0 eV tunneling electrons. CCH was selectively produced by terminating the voltage pulse upon detection of the current rise associated with HCCH to CCH conversion. CC was then produced from CCH by tunneling electrons with energies as low as 2.1 eV. Dissociation proceeded without diffusion, and hydrogen atoms could be imaged after dissociation as depressions with respect to the Cu(001) surface. Isotopic differences in dissociation thresholds were noted for HCCD and DCCD. These findings are summarized in Table I. At 0.2 eV below the threshold for single H(D) removal, diffusion, desorption, and simultaneous H(D) removal were observed for HCCH(DCCD), while the single H(D) removal channel was dominant at the quoted dissociation thresholds. The dissociation thresholds for HCCH and DCCD measured at 45 K were found to be 0.8 V higher.

The current changes which permit control over the dissociation can be understood by examining the constant current image cross sections shown in Fig. 2(b). The fourfold hollow site, and lateral tip position for dissociation, corresponds to the origin of the x axis (0 Å). Upon transformation of HCCH to CCH, the tunneling probability directly above the fourfold hollow site increases. This results in an increase in the gap distance Z for a fixed tunneling current [Fig. 2(b)] or an increase in current for a fixed gap distance [Fig. 2(a)]. Because the tunneling current is the only indicator of chemical evolution, a change in current level upon

TABLE I. The minimum observed dissociation thresholds of acetylene and ethynyl isotopes and the products of single bond scission. V_1 refers to the voltage required to create product 1 from the parent, and V_2 refers to the voltage required to create product 2 from product 1. The minimum dissociation threshold was determined by increasing the voltage in 0.1 V increments until dissociation was observed within 10 s at 1 nA. The variation in this threshold between tips was ~0.2 V. The dissociation rate was very sensitive to voltage; the HCCH dissociation rate increased approximately two orders of magnitude upon increasing the dissociating voltage 0.5 V.

Parent	V_1	Product 1	V_2	Product 2
HCCH	2.8	CCH	2.1	CC
HCCD	2.8	CCD	2.7	CC
DCCD	3.8	CCD	2.7	CC

the desired transformation is one requirement for this type of chemical control. An additional requirement of single H removal is that the lifetime of CCH being injected with 1 nA of 2.8 eV electrons must be longer than the time necessary to detect the initial dissociation event and terminate the pulse [12].

Using a method reported previously for acetylene [11], the rotational energy barrier of CCH between the four orientations [Figs. 1(c)–1(f)] was found to be 56 meV. For comparison, the rotational barrier of HCCH between its two orientations [Figs. 1(a) and 1(b)] was determined to be 169 meV [11]. Details of thermal and electron induced ethynyl rotation studies will be reported elsewhere [13].

The CCH and CCD fragments were further characterized by STM-IETS. The vibrational spectra of HCCH, DCCD, CCH, CCD, CC, and the copper background are shown in Fig. 3. The peak at 395(313) meV in the CCH(CCD) spectrum is assigned to the C-H(C-D) stretch. These peaks are up-shifted from the parent peak positions of 357 and 265 meV for HCCH and DCCD, respectively. No C-H or C-D related modes are evident in the CC spectrum. An electron-energy-loss spectroscopy (EELS) study of HCCH on Cu(001) determined a C-H stretch energy of 357 meV [14], in agreement with the STM-IETS value. In the same study, annealing of the sample led to the appearance of a peak at 375 meV which was attributed to the C-H stretch of the CCH species. The identity of the species responsible for this peak could not be unambiguously determined, however, and the authors allowed for the creation of CCH$_2$. The possibility that the STM-IETS measurement technique greatly influences the peak position seems unlikely as the energies of tunneling active modes observed to date are in general agreement with EELS values [4,7,15,16].

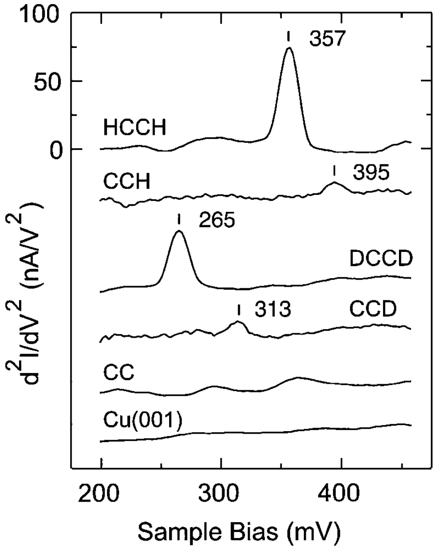

FIG. 3. Vibrational spectra of acetylene and ethynyl isotopes compared to those of CC and the bare copper surface. The C-H(C-D) stretch mode of CCH(CCD) is up-shifted and weakened compared to that of the parent HCCH(DCCD). The peak positions are indicated in meV. The spectra were taken under the following conditions: 1 nA and 0.25 V tunneling gap set point; 10 mV rms sample bias modulation at 260 Hz; 70 s scan time. The CCD spectrum is an average of 550 scans, the CCH an average of 400 scans, and the others are averages of 30 scans. Long averaging times were needed for the ethynyl species as the electron induced rotation introduces noise at all frequencies. The peak intensity of the particular CCH chosen for long signal averaging was anomalously low. Comparison with shorter scans on other CCH and CCD molecules suggests that the intensity ratio of ~1.4 for HCCH/DCCD also holds for CCH/CCD.

Prior to dissociation, HCCH, HCCD, and DCCD molecules were identified by their distinct vibrational spectra. The vibrational spectra of the products of HCCD and DCCD dissociation, created at 2.8 V and 3.8 V, respectively, were compared and found to be the same. This eliminates the possibility of CCD$_2$ formation, while the existence of a C-D stretch mode indicates that at least one D remains bonded to a carbon atom. Diatomic CD is ruled out by the fact that its dissociation product, atomic carbon, would not produce the azimuthal asymmetry in the images of the final dissociation product [Fig. 1(h)]. We therefore conclude that CCD(CCH) is the reaction intermediate. The end product CC can be converted back to CCH in a bimolecular reaction with a suitable choice of reactant [17], further confirming the molecular nature of the CC species.

The C-H stretch of CCH/Cu(001) (395 meV) is closer in energy to the gas phase value for HCCD (414 meV) [18] than that of HCCH/Cu(001) (357 meV). Similarly, the C-D stretch of CCD/Cu(001) (313 meV) is closer to that of the gas phase HCCD (320 meV) [18] than that of DCCD/Cu(001) (265 meV). This indicates that the C-C bond order increases toward the gas phase triple bond and that the interaction between the copper surface and CCH is significantly altered compared to HCCH. The lower rotational barrier of CCH is consistent with such a change, and the imaging data demonstrate a clear change in bonding geometry upon hydrogen loss in HCCH (Fig. 1).

The increased C-H stretch frequency of CCH compared to HCCH would suggest an increase in the C-H bond strength, yet the dissociation threshold is lower for CCH. This lower C-H threshold could result from an increase in the cross section for electronic excitation; the change in bonding may be accompanied by a shift in the electronic levels of the molecule. The threshold reduction could also be due to the reduced efficacy of molecule-metal relaxation channels. The dynamical evolution of acetylene excited by 3 eV electrons involves a competition between relaxation into the dissociation coordinate and relaxation into dissipative electronic and vibrational excitations of the substrate. To the extent that substrate dissipation is minimized, dissociation is more easily accomplished. This argument has been used in the context of electron stimulated desorption [19] and STM-induced desorption of hydrogen on silicon [20] and is also explanatory of the isotopic differences in dissociation thresholds [21]. Both electron-hole pair damping and phonon-assisted relaxation need to be considered. The electron-vibrational coupling is related to the gradient of the potential energy along the vibrational coordinate of interest and is expected to differ for acetylene and ethynyl given their distinct bonding geometries. In addition, the observed 0.8 eV increase in the acetylene dissociation threshold at 45 K suggests that multiphonon relaxation processes are involved in molecular deexcitation [22].

The ratio of the C-H stretch mode intensity of CCH/DCCH is 0.35, despite the fact that both species have one C-H bond. A change in the electron-vibrational coupling could be responsible for the intensity reduction [23]. As with the reduced rotational barrier and dissociation threshold, the lower STM-IETS intensity of CCH is consistent with a reduced coupling of the molecule to the surface. Some of the intensity change could also be due to a difference in the tip to C-H bond distance between the two species. During vibrational spectroscopy, the tip is positioned directly above the fourfold hollow site. For HCCD, this corresponds to the center of the molecule, but electronic structure calculations of CCH on Cu(001) indicate that CCH is displaced 0.3 Å along the [110] axis, resulting in a change in the amount of inelastic tunneling involving the C-H bond [24].

We have demonstrated a method to control sequential C-H bond breaking in an acetylene molecule. Because both the STM-IETS intensities and the dissociation thresholds depend on energy transfer between electronic and vibrational degrees of freedom in the adsorbate and surface, the results reported here have bearing on theories which attempt to describe excited states of molecules on surfaces. The experimentally determined adsorption structures, vibrational energies, and rotational barriers should assist in calculation of the ground state properties. The extension of these methods to other systems can lead to greater understanding of chemical dynamics at the atomic scale and the determination of molecular structures and energetics.

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