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Single-Molecule Chemistry and Analysis: Mode-Specific Dehydrogenation of Adsorbed Propene by Inelastic Electron Tunneling

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Supporting Information

ABSTRACT: A single propene molecule, located in the junction between the tip of a scanning tunneling microscope (STM) and a Cu(211) surface can be dehydrogenated by inelastic electron tunneling. This reaction requires excitation of the asymmetric C−H stretching vibration of the $=CH_2$ group. The product is then identified by inelastic electron tunneling action spectroscopy (IETAS).

Surface chemistry is governed by competing energy dissipation channels of vibrationally excited molecules.[1] On metal surfaces, excited molecular vibrations decay quickly via energy transfer to the substrate electrons by electron−hole pair formation. Alternatively, conversion into adsorbate dynamics (in the following referred to as *actions*) such as lateral translation, rotation, or dissociation can occur, but how the vibronic excitation of a molecule couples to these actions and which state-resolved excitations preferentially support them remains an open question. Adsorbate translations and rotations are fundamentally important, because they constitute the rate-limiting steps for reaction partners to meet. They are in competition with single molecule decomposition, and it is of interest to know which excited vibration leads to a certain motion or causes dissociation. Lifetimes of excited vibrations, determined by the efficiency of coupling between electronic and vibrational states, is connected to structural aspects of the adsorbate, like metallicity, adsorption site, and orientation of the adsorbent. Studying the decay pathways of excited molecules in connection with the structure of the adsorbate and the lifetimes of excited states contributes to a better understanding of the selectivity of surface chemical reactions.

Invented 30 years ago,[2] the scanning tunneling microscope (STM) has revolutionized surface science. Moreover, it has been developed as a tool for single molecule manipulations,[3] which go beyond repositioning of atoms and molecules for building artificial structures.[4] Nowadays, an STM allows time-resolved studies in the microsecond range by measuring the tunneling current versus time in the so-called open-feedback loop, that is, with the tip held stationary over the surface.[5] Hence, the STM actually provides an electron source with ultimate spatial resolution and current density. With a molecule in the tunnel junction, most of the electrons tunnel elastically, but a small fraction can tunnel inelastically by excitation of vibrational modes. This may then cause molecular surface dynamics, such as desorption,[6] dissociation,[7] chemical bond formation,[8] conformational changes,[9] rotation, and hopping.[10] Recently, we reported the manipulation of single propene molecules adsorbed on the copper(211) surface by inelastic electron tunneling (IET) as well as lateral pulling over the surface.[11] This induced rotation, hopping, and enantio-conversion.[11] Here, we present the IET-induced mode-selective dissociation of single propene molecules on Cu(211) and show that dissociation occurs only when the asymmetric C−H stretching mode of the olefinic $=CH_2$ group is excited. In addition, the reaction product is identified by IETAS, relating an action with a specific vibrational mode.

Propene has been adsorbed at 40 K on the intrinsically stepped Cu(211) surface under ultrahigh-vacuum conditions and cooled to 7 K in the STM. The Cu(211) surface consists of (111) terraces separated by (100) steps (Figure 1a). Its STM image is dominated by dark and bright stripes, the latter located on the (111) terrace near the step edge.[12] Two different types of propene adsorbates were identified; the methyl group points either toward the lower terrace or is located at the upper terrace.[11] DFT calculations showed that in both adsorbate configurations the molecules are bound with the C═C double bond on top of a step edge copper atom.[11] In addition, both configurations support two enantiomeric states, because the prochiral propene creates a chiral adsorbate upon adsorption.[13] Figure 1b shows two opposite enantiomers of protrusions with opposite tilt angles relative to the Cu(211) step edges (indicated by red dashed lines).

The procedure to induce a molecular response by IET has been described previously.[14] After imaging, the STM tip is positioned over a target molecule and the tunneling current is recorded as a function of time at a fixed bias voltage. A jump in current then indicates that an action has occurred, and rescanning of the same area reveals the nature of this action. In addition to translations and rotations induced at lower voltages and currents, high currents at sufficiently high bias voltages generate a new species, appearing in STM as elongated lobe aligned parallel to the steps (Figure 1c and Supporting Information). Note that the creation of such species does not change the appearance of propene molecules at other locations. Hence, the STM tip remains unchanged by this process. The product can still be manipulated, that is, a negative voltage pulse transfers the molecule to the STM tip, and subsequent scanning of the area

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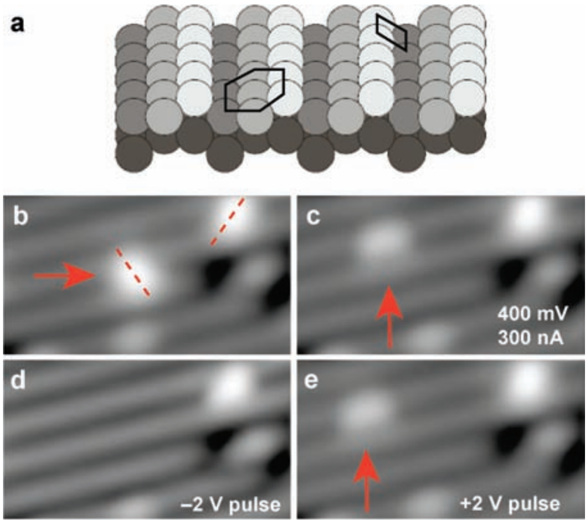

Figure 1. IET-induced decomposition chemistry of propene on Cu(211). (a) Model of an fcc(211) surface with (111) terraces and (100) steps, indicated by an hexagon and a square, respectively. (b) Tunneling electrons are injected into a single molecule (red arrow). (c) At 400 mV bias voltage and current of 300 nA, a new species is formed, which can be picked up by a negative voltage pulse with the tip. (d) Scanning of the same area does not show the product, because it is now located at the tip, and the STM contrast has improved. (e) Applying the opposite voltage pulse deposits the product back to the surface and the STM image shows the product again. Scanning parameters: 2.8 nm ×5 nm, U = 70 mV, I = 320 pA.

does no longer show the molecule in the image (Figure 1d). With the molecule at the tip, the STM contrast improved (Figure 1d). An opposite voltage pulse deposits the molecule back to the surface (Figure 1e). After such vertical manipulation, the product is always aligned parallel to the steps, while the vertical manipulation of propene leads always to the initially observed configurations.[11] We therefore conclude that the new species must be a product of a chemical reaction. Hydrogenation or oxidation of propene from species located at the tip can be excluded, because we were able to use the same tip with identical outcome for this manipulation for many times on different propene molecules. This leaves only dissociation as possible reaction.

The reaction rate R depends on the tunneling current as $R \propto I^N$, with N being the reaction order, that is, the number of electrons involved in the quantum mechanical excitation. We showed previously that actions like rotation and hopping of propene are first-order processes, while the inversion of the enantiomers is a second-order process.[11a] Because of insufficient time resolution, we could not determine the reaction rate here. However, the high currents needed suggest a multiple electron process. Basically, three distinct mechanisms must be considered for electron-induced dissociation, that is, either dissociation after electron attachment (negative ion resonance), electronic excitation, or vibrational excitation.[15] The possibility of electron attachment or an electronic excitation can be excluded here, because the energy levels of the lowest unoccupied molecular orbitals (LUMOs) of small physisorbed hydrocarbons are located a few electron volts above the Fermi level.[16] The bias voltages used here are too low (<400 mV) to allow tunneling into such states. Hence, the mechanism of excitation of propene occurs via vibrational heating. That means that the vibration is excited to levels of higher quantum numbers by a many-electron process (so-called ladder-climbing) until bond breaking occurs.

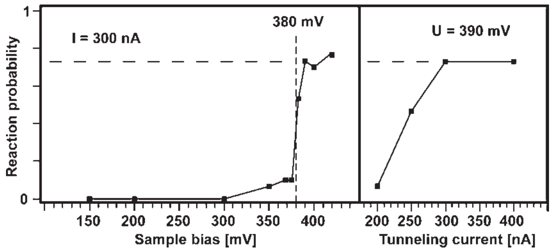

Figure 2. IET action spectrum for propene dissociation (left) and dependence of the reaction probability on tunneling current (right). Each data point results from at least 20 consecutive manipulation experiments. The threshold bias voltage for dissociation clearly correlates with the asymmetric C−H stretching mode of the olefinic CH_2 group.

It has been shown that the function of reaction probability versus bias voltage, the so-called action spectrum, is related to the vibrational density of states.[17] Figure 2 presents such action spectrum (I = 300 nA). At a bias voltage of 380 mV, the reaction probability increases sharply to 75%. Below 300 mV, no reaction was observed, while between 300 and 380 mV, a reaction probability of less than 20% was determined. For voltages larger than 380 mV, there is a 25% probability for other actions, such as hopping, rotation, and enantiomer inversion. We attribute the sharp step at 380 mV to the excitation into the first vibrational level of the asymmetric stretching vibration (ν_{as}) at the sp^2-CH_2 group. IR measurements show this vibration for propene on Cu(111) at 381.5 meV (3079 cm^{-1}).[18] From the currents needed for dissociation (Figure 2), one can also estimate the lifetime of the excited vibration, that is, it must be longer than 0.5 ps in order to allow multiple electron excitation. Note that ν_{as}-CH_2 is the highest-energy mode of adsorbed propene,[18] and only if this vibrational mode becomes excited, dissociation occurs.

In the following, we discuss possible products of the dissociation reaction. Previously performed IET-induced dissociations on similar molecules led to dehydrogenation instead of C−C or C−N bond cleavage.[19] Examples are the conversion of *trans*-2-butene to butadiene,[19a] C−H bond cleavage of acetylene to ethynyl (HC≡C−) and dicarbon (CC),[19b] and methylisocyanide formation from methylaminocarbyne by selectively breaking a N−H bond.[19c] Therefore, and because STM line profiles along the long molecular axis of the product do not suggest a shorter entity here (Supporting Information), we assume an IET-induced dehydrogenation as dissociation reaction. Consequently, products like allene (propadiene, $H_2C{=}C{=}CH_2$) or propyne ($CH_3{-}C{\equiv}CH$) must be considered. Because the product could still be manipulated laterally and vertically, we exclude a radical like $CH_3{-}CH{=}CH\cdot$. Such entity would be too strongly bound to the surface, thus, preventing vertical manipulation.

Previously, single-molecule IET dissociation products have been identified with IET spectroscopy (IETS).[19] The change in tunneling current due to excitation of vibrations via IETS thereby allows molecular vibrations to be directly monitored.[3] However, our attempts to directly identify vibrations via IETS were not successful. IETS relies on conductance change, and often the elastic tunneling channel changes simultaneously with opposite sign to the inelastic channel, thus, canceling the signal.[20] In our case, however, the reaction product can still be further manipulated by IETAS. Figure 3 shows the IET-induced hopping of the

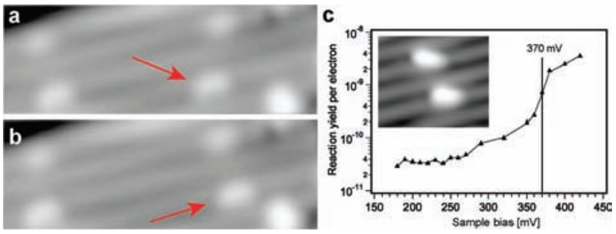

Figure 3. IET action spectroscopy performed with the dissociation product. Injection of tunneling electrons (a) causes the molecule to jump parallel to the step edges (b). The hopping rate increases substantially when the threshold of 370 mV is exceeded (c). The STM image in panel c shows propyne for comparison. Scanning parameters a and b, 2.2 nm ×6.4 nm U = 70 mV, I = 320 pA; c, 3.2 nm ×3.7 nm, U = 70 mV, I = 1.2 nA.

product. The molecule jumps one lattice constant on the terrace parallel to the step edge. This action correlates with the excitation of a vibration at 370 meV (2984 cm^{-1}) and fits best to a $=CH_2$ symmetric stretching vibration (ν_s) at 2980 cm^{-1},[18] as existing in allene. Considering the resolution of the action spectrum in Figure 3c, also the ν_{as} mode of a methyl group at 2940 cm^{-1} of propyne could cause this action. We adsorbed propyne directly from the gas phase in order to distinguish between these two possibilities. Its STM appearance is completely different than that of the IET-reaction product (Figure 3c and Supporting Information). One can actually distinguish between the two different ends of the molecule. As in the case of propene and 1,3 butadiene,[11,14] the methyl group seems to dominate the STM appearance. On the basis of the difference of STM appearance of propyne and product, together with the better match of the action spectrum with a symmetric C−H stretching vibration in the $=CH_2$ group, we conclude allene as IET-induced dehydrogenation product of propene.

We note that only excitation of ν_{as} leads to dissociation and attribute this mode-selectivity to shorter lifetimes of all other vibrations. This suggests that only ν_{as}-CH_2 has a sufficiently long lifetime to allow vibrational heating, that is, a multielectron ladder-climbing process.[21] Moreover, it is noteworthy that the dehydrogenation occurs away from the site of the excited vibration. This differs from previous IET-induced reaction work.[19]

In conclusion, we have shown that vibrational heating of single propene molecules by inelastically tunneling electrons leads to dehydrogenation only after excitation of the asymmetric C−H stretching mode at the $=CH_2$ group. The product was identified by inelastic electron tunneling action spectroscopy, correlating hopping of the molecule with the excitation of the symmetric C−H stretching vibration of a $=CH_2$ group and by exclusion of propyne as product. This leaves allene ($H_2C=C=CH_2$) as IET dehydrogenation product. Hence, we performed single-molecule chemistry and single-molecule chemical analysis on educt and product, respectively. For molecules adsorbed on small metal clusters on thin oxide films, different lifetimes of excited vibrations and different chemistry must be expected. Extending our studies to such model systems will consequently provide fundamental insight into chemical selectivity in heterogeneous catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. STM images and line profiles of propane, propene, propyne and the IET product on Cu(211). This material is available free of charge via the Internet at http://pubs.acs.org.

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