How Stereoselective Are Alkene Addition Reactions on Si(100)?

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There has been considerable recent interest in the covalent attachment of organic molecules to silicon surfaces using both ultrahigh vacuum and wet chemical approaches.[1,2] This interest is largely motivated by the desire to integrate the wide range of available functionalities of organic molecules with existing microelectronics technology. As the properties of these ultrathin films will depend on details of their structure it is necessary to develop methods for probing and controlling not only the placement of the molecules on a surface, but their orientation and conformation as well. In this context reactions in which the molecules retain their geometric configurations upon reaction with the surface are particularly desirable. The addition of alkenes to the dimers of the reconstructed Si(100) surface have been suggested as an example of such a stereospecific reaction.[3,4] These reactions are facile, resulting in the formation of two Si−C bonds as in a formal [2 + 2] cycloaddition[5−9] and have been exploited to controllably attach a number of different molecules to the Si(100) surface.[10−12]

Previous studies of the stereochemistry of alkene addition, using macroscopic techniques, have concluded that the alkenes retain their stereochemistry upon adsorption.[3,4] However, the limited sensitivity of the techniques used did not allow small amounts of isomerization (<5%) to be detected. Previously we have demonstrated that scanning tunneling microscopy (STM) is a uniquely powerful probe of the degree of stereoselectivity of surface reactions, with the sensitivity simply determined by the number of molecules examined.[13] Here we report that, applying this technique to monitor the addition of *cis*- and *trans*-2-butene to the Si(100) surface, a small but measurable degree of isomerization is observed indicating that this reaction, while highly stereoselective, is not stereospecific.

The STM studies were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below 5×10^{-11} Torr. This pressure is sufficiently low to maintain a clean surface for a day or more. A clean Si(100) surface was obtained by flashing a well-degassed crystal (Virginia Semiconductor, n-type, 0.005 Ω cm) above 1200 °C. The samples were exposed to 2-butene (purity 99+%) by controllably leaking the gaseous molecules into the vacuum chamber. The gases were analyzed by both NMR and gas chromatography and the isomeric purity was determined to be 99.8 ± 0.1% for both *cis* and *trans* samples.

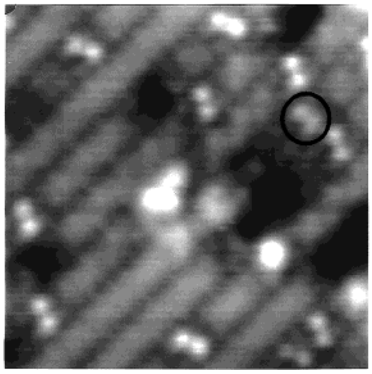

Figure 1. Unoccupied state STM image (75 Å × 75 Å, 2 V, 40 pA) of a Si(100) surface exposed to *trans*-2-butene. While most of the molecules retain their configuration upon adsorption, the circled molecule has undergone isomerization to the *cis* form.

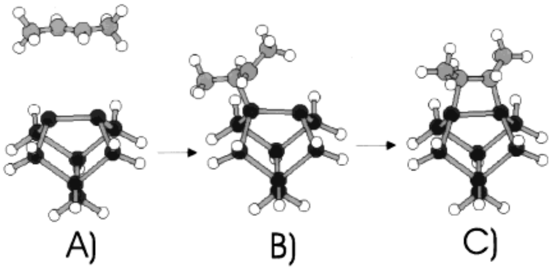

Figure 2. The steps involved in the reaction of a *trans*-2-butene molecule with a dimer on the Si(100) surface; (a) molecule approaches surface, (b) radical intermediate, (c) [2 + 2] product.

Figure 1 shows an unoccupied state STM image of a Si(100) surface exposed to a flux of *trans*-2-butene molecules. The bar-like structures running diagonally across the images are the dimer rows of the clean Si(100) surface. The dimers are 3.84 Å apart and the rows are separated by twice that distance. The various dark features are defects. The butene molecules are imaged as paired protrusions, centered along a dimer row. Comparison with the calculated bonding geometry (see Figure 2c) reveals these protrusions to be due to the two methyl groups on either end of the molecule.[13] For the large majority of the adsorbed molecules, the two protrusions define a line that is inclined by ~30° with respect to the dimer row direction—consistent with an adsorbed molecule that has retained its configuration upon adsorption. However, a small fraction of molecules, an example is indicated in Figure 1, exhibit protrusions which define a line perpendicular to the dimer row direction, just as observed when the *cis* isomer has been adsorbed on the surface. By examining several hundred molecules, the fraction of molecules in the *cis* configuration is determined to be 2.1 ± 0.7%. This is measurably higher than the level of *cis* contamination of the *trans*-2-butene gas sample, determined to be 0.2 ± 0.1%. A similar analysis of images after exposure to *cis*-2-butene, indicates that 2.6 ± 0.6% of the adsorbed molecule are in the *trans* geometry. These observations indicate that, while the adsorption of the 2-butenes is highly stereoselective, it is not stereospecific, with approximately 2% of the molecules undergoing isomerization upon adsorption. The STM images also show that isomerization occurs at dimers of the clean surface and is not induced by defects, steps, or interactions with other adsorbates.

The current observations are not inconsistent with previous studies which concluded that alkene addition on Si(100) is

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stereoselective. Kiskinova and Yates showed that samples exposed to *cis* and *trans*-2-butene exhibit distinctly different desorption energies, demonstrating that most of the molecules retain their configuration upon adsorption.[3] In a related study Liu and Hamers compared measured and calculated splitting of the C−H stretch modes to conclude that dideuteroethylene adsorption was also stereoselective.[4] Both these studies, however, employed macroscopic techniques not sufficiently sensitive to detect the small levels of isomerization described here.

The desorption study of *cis*- and *trans*-2-butene revealed that the adsorbed *trans* isomer is 4 kcal/mol more stable than the *cis* species.[3] It is notable then, that *if* the molecules could equilibrate, we would expect almost complete isomerization of the *cis* molecules, while virtually all of the *trans* molecules would retain their configuration. As the degree of isomerization reported here is similar for both the *trans* and *cis* isomers, we may conclude that the process is kinetically rather than thermodynamically controlled.

Our observation that a small but statistically significant fraction of the adsorbing 2-butene molecules isomerize has implications for the mechanism of alkene/Si(100) [2 + 2] addition reactions. Before discussing those, we note the possibility that isomerization occurred *before* adsorption on the silicon surface has been considered and found not to be supported by our measurements. Our reasoning is straightforward. The stainless steel gas-handling vacuum systems used in preparation for NMR and gas chromatographic as well as for STM experiments were equivalent. Since the STM measurement alone showed relatively high isomer contamination, we conclude that the factor unique to that measurement, the silicon surface, was responsible for the observed isomerization.

The first conclusion to be drawn from the observation of isomerization upon adsorption is that a completely concerted addition along a symmetric pathway is ruled out, as that would require strict retention of the stereochemistry. Such a concerted [2 + 2] cycloaddition reaction of a symmetric dimer with an alkene is formally forbidden by Woodward−Hoffmann rules. However, the dimers are in fact buckled, with the "up" end of the dimer becoming electron rich and the "down" atom electron-deficient.[14,15] While this buckling breaks the symmetry and lifts this restriction, it also suggests that the reaction is likely to occur via an asymmetric path[16,17] and be stepwise rather than concerted, allowing for the possibility of isomerization upon adsorption. It is likely that adsorption proceeds via a single Si−C bonded radical species, as shown in Figure 2. A stepwise reaction mechanism allows for rotation about the central C−C bond. Within this model, the amount of isomerization will depend on the relative time-scales for rotation about the C−C bond versus formation of the second Si−C bond, closing the four-membered ring. If the probability of undergoing a rotation before the second bond is formed is high, a large degree of isomerization is expected, leading to an equal number of the two configurations on the surface. Observation of only a small degree of isomerization indicates that the second bond is formed relatively rapidly, allowing only a small probability of crossing the C−C bond rotational barrier before the ring is closed. The measured isomerization rate indicates that ∼2% of the molecules execute a rotation before the second Si−C bond is formed. Assuming a barrier of 4 kcal/mol (typical for rotation about a single C−C bond) and a prefactor of 10^{13} s^{-1}, the time between the formation of the two bonds can be estimated to be ∼2 ps.

In the absence of a barrier to formation of the second Si−C bond, the degree of isomerization should increase rapidly as the adsorption temperature is raised, increasing the probability of surmounting the rotation barrier before the ring closes. For a rotational barrier of 4 kcal/mol the degree of isomerization is predicted to increase to 5.7% at 350 K (assuming the prefactor remains constant). In contrast, the level of isomerization of the *cis*-2-butene is measured to be 2.1 ± 0.5% for adsorption at 350 K. This is within the error bars of the 2.6 ± 0.6% isomerization probability for room temperature adsorption, indicating a rather weak temperature dependence. The weaker than expected temperature dependence points to a deficiency in our simple model. It is most likely that a barrier, comparable to that for rotation about the C−C bond, exists for closing of the ring − this will include contributions related to rotation about the Si−C bond and to formation of the second Si−C bond once alignment is achieved. If ring closing is activated, this will compensate for more facile rotation about the C−C bond at elevated temperature. This scheme can account for either a weak increase or decrease in isomerization with increasing temperature (both consistent with the current data), depending on the relative heights of the two barriers. The present data yields an upper limit on the difference in barrier heights, with the barrier for ring closing less than 1 kcal/mol smaller or 2.6 kcal/mol larger than the rotational barrier. More detailed studies are required to determine the direction and magnitude of the temperature dependence. Theoretical calculations can also provide useful insight into the relative heights of these barriers. Although there are, as yet, no available calculations of the reaction pathway for 2-butene addition to Si(100), calculations for acetylene[16] and ethylene[18] addition via a radical intermediate state yield barriers to ring closure of 4.6 and 2 kcal/mol, respectively. These studies did not calculate rotational barriers in the radical state.

Before closing, we note that an alternate scenario can also account for the observed weak temperature dependence of isomerization. As energy relaxation on semiconductor surfaces is often inefficient, it is possible that the energy released upon reaction is converted solely into internal energy of the adsorbate. Forming the single Si−C bonded species is calculated to liberate approximately 10 kcal/mol (5000 K) of energy, some of which can be converted into the relevant rotational mode which drives isomerization. If this rotational temperature is higher than the substrate temperature, the isomerization rate would be temperature-independent. This would also reduce our estimate of the time-scale for formation of the second Si−C bond. Although equipartition of the adsorption energy among all of the modes of the adsorbate would suggest the temperature of the relevant rotational mode would be less than 166 K, it is possible that individual molecules could have a rotational temperature considerably higher than this.

In conclusion, we have used scanning tunneling microscopy to study the degree of stereoselectivity of the reaction of 2-butene with the Si(100) surface. A small degree of isomerization is observed, indicating that the reaction, although 98% stereoselective, is not stereospecific. This implies that the [2 + 2] cycloaddition reactions of alkenes on this surface proceed in a stepwise manner with the time scale between formation of the two Si−C bonds on the order of a few picoseconds. These results also have implications regarding the extent to which molecular conformation can be controlled in organically modified surfaces made via this approach. More generally, this study demonstrates the usefulness of STM in monitoring the stereochemistry of surface reactions at the single-molecule level.

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