Cycloaddition Chemistry of 1,3-Dienes on the Silicon(001) Surface: Competition between [4 + 2] and [2 + 2] Reactions

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The reactions of 1,3-dienes with the Si(001) surface have been investigated using scanning tunneling microscopy (STM) and Fourier transform infrared spectroscopy (FTIR), and the relative efficiencies of [2 + 2] and [4 + 2] reactions have been determined. STM and FTIR studies show that the 2,3-dimethyl-1,3-butadiene molecule has two bonding configurations; 80% of the molecules bond via a [4 + 2] reaction involving both alkene groups with the remaining 20% bonding via a [2 + 2] reaction involving only one alkene group. The molecule 1,3-cyclohaxadiene shows three separate bonding configurations in the STM, and the FTIR shows at least four separate peaks in the alkene stretching region. The [4 + 2] product is found to comprise 55% of the surface species, the [2 + 2] product 35%, and an unknown product 10%. The surface temperature is found to have little affect on the product distribution. The formation of multiple products and the lack of temperature effects indicate that the product distribution is controlled primarily by the kinetics of the adsorption process, not by the thermodynamics. Thus, although [4 + 2] reactions are predicted to be more stable, [2 + 2] reactions occur nearly as frequently.

Introduction

The reaction chemistry of the silicon surface has been an area of intense research for over three decades.[1] The chemistry of the (001) face has been of particular interest because it is the starting point for almost all silicon-based microelectronics. When a silicon crystal is cleaved along the {001} plane, each Si surface atom is left with two bonds to the bulk and two "dangling bonds" with one electron in each. This cleavage results in a 2 × 1 reconstruction in which two adjacent Si atoms pair together. Both theoretical[2] and experimental[3,4] studies indicate that, to a first approximation, the bonding can be described in terms of a strong σ and a weak π bond. However, because of the strained geometry at the surface, the π overlap of the Si surface dimers is poor. As a consequence, the π bond is very weak and the Si(001) surface is very reactive.[1,5] Additionally, dynamic tilting of the dimers leads to time-dependent charge transfer between the dimer atoms, introducing some zwitterion-like character.[3,4,6]

It has been known for some time that some unsaturated hydrocarbons (alkenes) can attach to the Si(001) surface via the interaction of the π bond of the alkene with the π bond of a Si=Si dimer on the surface, producing two new Si−C σ bonds.[7−14] More recently, we have shown that by using cyclic alkenes, it is possible to form organic layers in which the molecules adsorb into a highly ordered array, producing "epitaxial" organic monolayers.[15−19] The reactions are analogous to a class of reactions known in the organic chemistry literature as [2 + 2] cycloaddition reactions, which involve the breaking of two π bonds and the formation of two new σ bonds. The concerted "suprafacial" interaction of two alkenes, in which the two π bonds are broken as the new σ bonds are formed, is forbidden by symmetry considerations; consequently, the reactions typically occur very slowly either through nonconcerted processes (diradical formation, for example) or through a photochemical process via an excited electronic state.[20,21] Similar reactions of disilenes (compounds containing Si=Si

double bonds) have found [2 + 2] reactions to be extremely slow.[22,23] In contrast, the analogous [2 + 2] reactions between the Si(001) dimers and alkenes are very facile, occurring at room temperature with reaction probabilities of near unity.

A second class of cycloaddition reactions widely known in organic chemistry is the [4 + 2] or "Diels-Alder" reaction between a conjugated dialkene (diene) and an alkene. Diels−Alder reactions produce a six-membered ring containing one residual C=C bond. In the analogous [4 + 2] reaction between a diene and a Si=Si surface dimer, the 1,4-carbon atoms of the diene bond to the Si=Si dimer and the remaining electron on the 2,3-carbon atoms form a new C=C π bond. Because this [4 + 2] reaction produces a six-membered Si_2C_4 ring at the interface while the [2 + 2] reaction produces a more highly strained four-membered Si_2C_2 ring, the [4 + 2] reaction is expected to produce the more stable product. For adsorption of 1,3-cyclohexadiene on Si(001), for example, the [4 + 2] product has been predicted[24] to be more stable than the [2 + 2] product by 15.2 kcal/mol. Recent experimental results[25,26] for adsorption of 2,3-dimethyl-1,3-butadiene and 1,3-butadiene on the Si(001)-2 × 1 surface have also reported evidence only for the [4 + 2] product.

The formation of ordered organic layers on the Si(001) surfaces requires adsorption into a unique bonding geometry, as the presence of more than one bonding configuration almost always leads to disordered layers. For organic reactions between an alkene and a diene, the [2 + 2] reactions are very slow and the [4 + 2] reactions are moderately facile, so that the [4 + 2] coupling reactions are quite selective. For the analogous surface reactions, however, we have observed that the [2 + 2] reactions are facile. This suggests that the [4 + 2] reactions, while in principle leading to the more stable product, might not be very selective when occurring on the Si(001) surface. In this paper, we investigate the competition between the [4 + 2] and [2 + 2] reactions at the Si(001) surface.

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Experimental Section

All experiments were performed in ultrahigh vacuum (UHV) systems. The scanning tunneling microscopy (STM) images were obtained using a home-built instrument with tunneling currents of 150−200 pA and sample biases of −2.2 to −2.4 V. The Fourier transform infrared (FTIR) spectra were obtained using a multiple internal reflection geometry, as described previously,[27] with 2 cm^{-1} resolution. For each experiment, samples were prepared and characterized completely in situ.

The 2,3-dimethyl-1,3-butadiene was purchased from Aldrich 98% pure, while the 1,3-cyclohexadiene was purchased from Aldrich 97% pure. Both molecules were subjected to repeated freeze−pump thaw cycles and checked for contamination in situ using mass spectrometry. For both the STM and FTIR experiments, a directed doser was used to minimize interactions with the chamber walls; as a result, the actual pressure at the sample is higher than the chamber pressure. Since these should be proportional to one another, however, chamber pressure was utilized as a measure of the overall sample dose. All exposures reported in this paper are nominal exposures based on the background pressure in the chamber.

The clean Si(001) samples were prepared by flash annealing pieces of Si(001) wafers at 1475 K, while the chamber pressure was kept under a pressure of 3×10^{-10} Torr. This procedure is well-known to produce clean, well-ordered surfaces exhibiting a 2 × 1 reconstruction.[3] The STM experiments use highly doped (<0.15 ohm-cm resistivity, Sb-doped) "on-axis" Si(001) samples. On-axis samples contain a mixture of two equivalent domains of dimer orientations, rotated by 90° with respect to one another. The FTIR experiments used both lightly doped (>5 ohm-cm resistivity, P-doped) "off-axis" or "vicinal" Si-(001) samples and lightly doped (>5 ohm-cm, B-doped) "on-axis" Si(001) samples. Vicinal samples are miscut off the ⟨001⟩ axis by 4° toward the ⟨1$\bar{1}$0⟩ direction; on these samples the dimers are all oriented in the same direction across the entire sample, thereby permitting polarized IR light to probe the infrared transition dipole components along different dimer orientations.[28]

Results

The first molecule to be examined here is 2,3-dimethyl-1,3-butadiene (DMBD). Figure 1 shows two STM images taken after the Si(001) surface was exposed to 0.1 Langmuir (1 × 10^{-8} Torr for 10 s) of DMBD. The images were acquired with a tunneling current of 200 pA and a sample bias of −2.4 V. In the top image, an atomic height step can be seen running horizontally across the surface. The STM images show two different protrusions on the surface; the brighter protrusions are labeled A and the dimmer ones are labeled B. The complex appearance of these features is immediately striking. Because such complex structure can result either from the internal structure of the adsorbed molecules or from an atomic-scale structure of the STM probe tip, we repeated these STM experiments several times. In all cases we observe the centroid of the features at the same location with respect to the underlying Si=Si dimers, but the details of the apparent internal structure were not completely reproducible. Attempts to image the surface at saturation coverage failed to yield any consistent ordered structure.

At low coverage, the locations of these features with respect to the underlying Si(001) dimers could be identified, as depicted at the bottom of Figure 1. The A features are centered on top of a dimer row with the centroid midway between two Si=Si dimers. The B features are located in the troughs between dimer
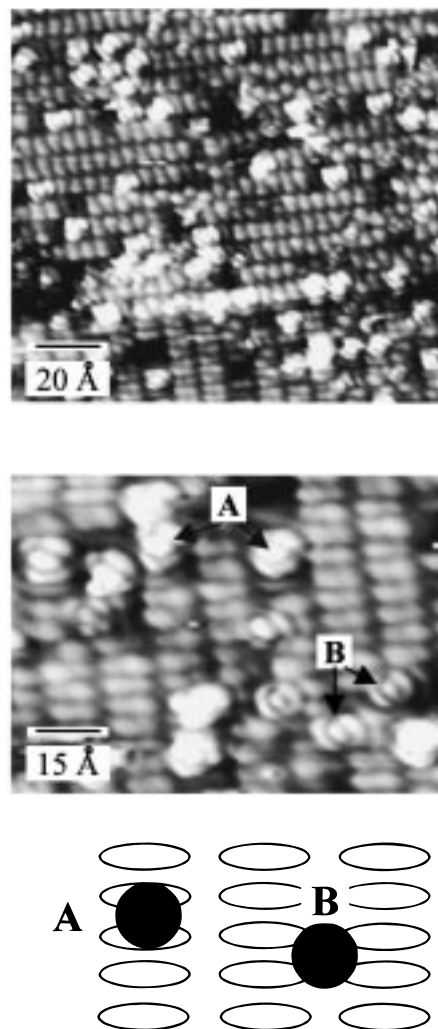

Figure 1. STM images showing the Si(001) surface after it was exposed to 0.1 Langmuir of 2,3-dimethyl-1,3-butadiene at room temperature, and a schematic illustration showing the position of the adsorbates with respect to the underlying dimers. The images were acquired with a tunneling current of 200 pA and a sample bias of −2.4 V.

rows with their centroid midway between two dimers. Counting statistics show that the A protrusions comprise ∼80% of the adsorbed molecules, and the B protrusions comprise ∼20% of the adsorbed molecules.

To help identify the chemical form of the A and B species, we conducted infrared absorption experiments, as shown in Figure 2. The upper spectrum was obtained after a clean Si-(001) surface was exposed to 0.1 Langmuir (1 × 10^{-8} Torr for 10 s) of DMBD at room temperature using a two-domain sample and unpolarized light. In this spectrum the features group into three different regions. The 2750−3000 cm^{-1} region shows a strong, broad absorbance; this region is where C−H stretches of saturated hydrocarbons are typically observed. Although the peaks here are not well-resolved, there is clearly one primary peak at 2910 cm^{-1} and smaller peaks near 2862 and 2955 cm^{-1}. A weaker stretch is observed at 3090 cm^{-1}, which is the region where vinylic (C=C−H) stretches are typically observed. Finally, there is a small amount of absorbance in the 2000−2150 cm^{-1} region, where Si−H stretching vibrations are typically observed. For comparison, the lower spectrum in Figure 2 shows the FTIR spectrum of a DMBD "ice", prepared by cooling the sample to 100 K and then exposing it to 100 Langmuirs of 2,3-dimethyl-1,3-butadiene (DMBD). In the ice

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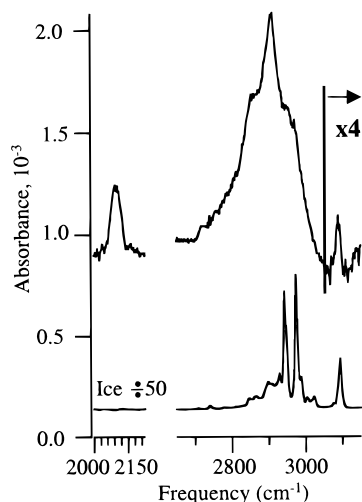*J. Phys. Chem. B, Vol. 102, No. 35, 1998* **6875**

Figure 2. FTIR spectra of the Si(001) surface after the adsorption of 2,3-dimethyl-1,3-butadiene. The top spectrum was taken after 0.1 Langmuir exposure at room temperature; a two-domain sample and unpolarized light were used. The bottom spectrum shows an ice of DMBD created by exposing the surface to 100 Langmuir at 100 K.
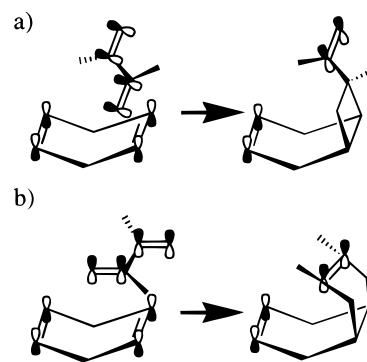

Figure 3. Schematic illustration of the interaction of 2,3-dimethyl-1,3-butadiene with the Si(001) surface. (a) [2 + 2] interaction of one 2,3-dimethyl-1,3-butadiene C=C bond with a Si=Si dimer. (b) [4 + 2] interaction of both 2,3-dimethyl-1,3-butadiene C=C bonds with a Si=Si dimer.

the molecules are oriented randomly, while on the Si(001) surface they are not. Consequently, it is not possible to quantitatively compare the intensities of the two spectra. However, we note that the ice spectrum shows a large peak at 3093 cm^{-1} (in the C=C−H stretching region) close to the 3091 cm^{-1} observed for chemisorbed DMBD. The ice shows other intense peaks at 2976 and 2939 cm^{-1}. We note that the submonolayer DMBD/Si(001) spectra shows substantially greater absorbances at lower frequencies (2800−2900 cm^{-1}) than the DMBD ice does.

To identify the bonding configuration of DMBD, we first note that the presence of Si−H vibrations suggests the possibility of partial dissociation upon adsorption. The Si−H transition dipole is significantly stronger than that of the C−H modes. To more quantitatively determine the extent of possible dissociation, we measured, in the same apparatus using samples of identical size, the absorption of the Si(001)−(2 × 1)H "monohydride" surface prepared by exposing the clean Si(001)− (2 × 1) surface to atomic hydrogen produced by thermal dissociation on a hot filament.[29] The integrated absorbance of the monohydride surface, which contains one hydrogen atom per surface silicon atom, was 0.13 cm^{-1}. Integrating the area of the Si−H peak in the sample spectrum in Figure 2 yields a value of 0.0060 cm^{-1}. This then corresponds to a surface hydrogen coverage of 0.04 monolayer for a surface saturated with DMBD. This is an upper limit on the amount of dissociation because some of the hydrogen atoms are due to the adsorption of water or other contaminates. Indeed, in repeated experiments we find that the amount of surface hydrogen varies from sample to sample while the C−H region remains identical; this suggests that the small amount of surface hydrogen detected in the FTIR arises from trace contaminants in the chamber or, more likely, in the reactants themselves. We additionally note that neither the A nor the B species has the proper symmetry to be accounted for by individual H atoms, paired H atoms on a single dimer,[30−32] or methyl group,[33] all of which have been studied previously via STM. Thus, we conclude that the vast majority of impinging DMBD molecules adsorb without C−H or C−C bond cleavage and that adsorption occurs primarily through interaction of one or more of the C=C bonds with the surface dimers.

While the complexity of the 2750−3000 cm^{-1} region precludes extracting much information about the molecular

binding, we note that the presence of a vinylic C−H stretch at 3093 cm^{-1} has important implications. If all the molecules reacted via a [4 + 2] "Diels−Alder" reaction, this peak should have completely disappeared. The presence of this peak, therefore, implies that not all molecules react via the [4 + 2] pathway. We note that although previous researchers did not observe the 3093 cm^{-1} peak in their infrared spectra,[25,26] a comparison of the previously published spectra with that shown in Figure 2 indicates that our signal-to-noise ratio is higher, allowing us to observe a peak that would have been unobservable in the previous studies.

For DMBD on Si(001), our FTIR data show that there is no significant C−H bond cleavage and that the surface products show some vinylic C−H stretch, an absorbance which would be completely absent for the product formed by the [4 + 2] reaction. Likewise, STM images show that there are two products formed, clearly distinguishable by having different bonding locations with respect to the underlying Si=Si dimers. Figure 3 schematically depicts the products of the [2 + 2] (Figure 3a) and [4 + 2] (Figure 3b) reactions. The A-type protrusions lie within a dimer row, encompassing the area of two dimers with their midpoint roughly between the dimers. A comparison with Figure 3b indicates that this symmetry would be expected for the product of the [4 + 2] reaction. The B type protrusions lie in the troughs between dimer rows; this bonding location is consistent with the product produced by reaction of only one C=C bond with a Si=Si dimer via a [2 + 2] reaction, as shown in Figure 3a. Therefore, we conclude from the STM and FTIR data that at 300 K DMBD bonds to the surface through a [4 + 2]-type reaction 80% of the time, leading to the A features, and through a [2 + 2]-type reaction 20% of the time, leading to the B features.

Efficient reaction via a [4 + 2] reaction can only be accomplished if the reactant is in a cis configuration. While DMBD can convert readily between cis and trans configurations, for cyclic dialkenes the molecular configuration can be held in the cis configuration. To this end, we also investigated the adsorption of 1,3-cyclohexadiene (1,3-CHD) using STM and FTIR. Figure 4 shows infrared spectra acquired after the Si-(001) surface was exposed to 1,3-CHD at room temperature. The bottom two spectra were obtained using polarized light and single-domain samples, with a 1,3-CHD exposure of 5 Langmuirs (saturation coverage). The top spectrum was obtained after only 0.1 Langmuir exposure (subsaturation coverage); to obtain the best signal-to-noise ratio, this spectrum was obtained using unpolarized light on a two-domain sample. The large absorbance in the C−H stretching region and the absence of
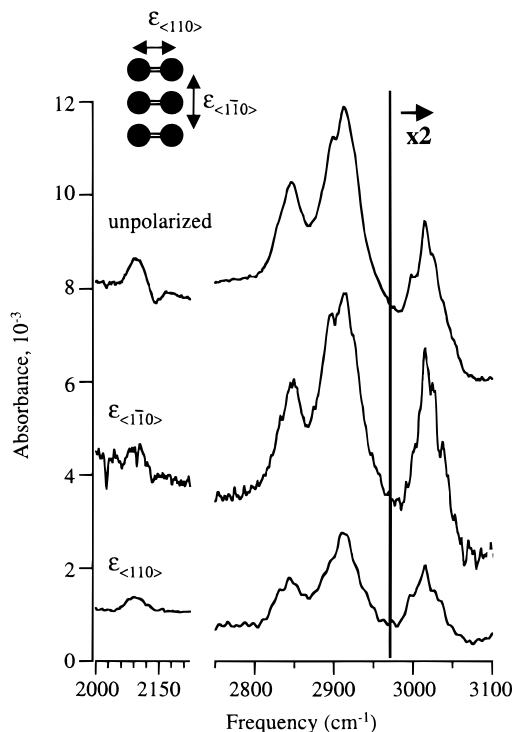
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Figure 4. FTIR spectra of the Si(001) surface after the adsorption of 1,3-cyclohexadiene at room temperature. A two-domain sample and unpolarized light were used for the top spectrum; the exposure was 0.1 Langmuir. A single-domain sample and s-polarized light, with the dimer orientation indicated in the figure, was used for the bottom two spectra, the exposure was 5 Langmuir.

any significant absorbance in the Si−H stretching region indicate that the molecules have adsorbed molecularly. While our previous investigations of organic molecules adsorbed on Si-(001) have generally shown sharp C−H vibrational structures, we see in this case that the alkene C−H stretching region, in particular, is rather broad. Underneath this broad envelope, however, one can identify at least four separate peaks at 2997, 3015, 3026, and 3038 cm^{-1}. The spectral region above ~3000 cm^{-1} arises almost entirely from alkene C−H stretches; since each alkene group has two attached hydrogens, the presence of four peaks here indicates the presence of at least two distinct products on the surface.

Figure 5 shows two STM images of the Si(001) surface after exposure to 0.1 Langmuir (1×10^{-8} Torr for 10 s) of 1,3-CHD at room temperature. The images were acquired with a tunneling current of 150 pA and a sample bias of −2.2 V. The top image has an atomic height step running vertically through the image. Three separate protrusions are visible in these images, labeled A, B, and C. Counting statistics show that the A-type protrusions comprise 55% of the protrusions, the B-type 10%, and the C-type 35%. The A-type protrusions are somewhat diffuse in appearance, making it difficult to determine their symmetry with respect to the underlying surface. They appear to be centered above the dimer. The B-type protrusions are elongated objects parallel to a Si≡Si dimer, and the C-type protrusions are small round objects contained within a dimer row but offset from the center. These bonding locations are depicted schematically in Figure 5. Thus, our STM data clearly shows that there are at least two, and possibly three, significant bonding configurations for 1,3-CHD on the Si(001) surface.

To further assist in understanding the role thermodynamics and kinetics play in the reactions, we investigated the effect of thermal annealing on the bonding of 1,3-CHD to Si(001). Figure 6 shows the result of annealing on the surface structure.
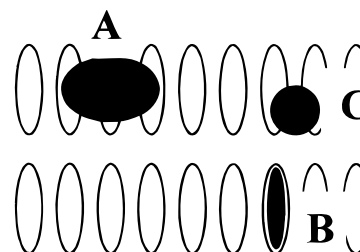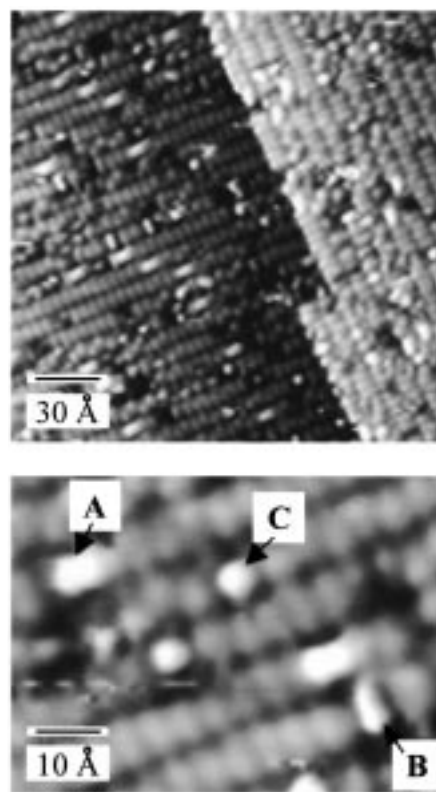

Figure 5. STM images showing the Si(001) surface after it was exposed to 0.1 Langmuir of 1,3-cyclohexadiene at room temperature, and a schematic illustration showing the position of the adsorbates with respect to the underlying dimers. The images were acquired with a tunneling current of 150 pA and a sample bias of −2.2 V.
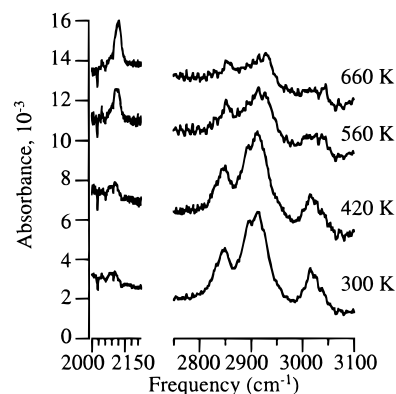

Figure 6. FTIR spectra of the 1,3-cyclohexadiene-saturated Si(001) surface heated to the temperature indicated; the spectra were all acquired at room temperature. The initial surface was prepared by exposing a single-domain Si(001) surface to 5 Langmuir at room temperature. s-Polarized light was used for all the spectra with the direction of the electric field being perpendicular to the dimer axis.

The surface was prepared by first annealing clean, single-domain Si(001) samples to prepare the dimerized (2×1) surface; the

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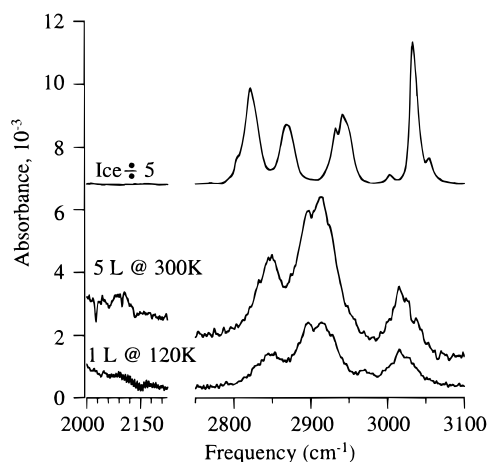*J. Phys. Chem. B, Vol. 102, No. 35, 1998* **6877**

Figure 7. FTIR spectra of the Si(001) surface after the adsorption of 1,3-cyclohexadiene. The top spectrum shows an ice of CHD created by exposing the surface to 10 Langmuir at 100 K. The bottom two spectra were taken after exposing the surface to 5 Langmuir at 300 K and 1 Langmuir at 120 K, respectively. Single-domain samples and s-polarized light were used for the bottom spectra; the direction of the electric field was perpendicular to the dimer axis.

surface was then exposed to saturation coverage (5 L) of 1,3-CHD at 300 K followed by annealing to the specific temperature for 2 min. All spectra were acquired at 300 K. For these spectra, s-polarized light was used with the electric field directed along the $\langle 1\bar{1}0 \rangle$ direction, perpendicular to the Si=Si dimer bond axis. Figure 6 shows that annealing to 420 K produces almost no change in the infrared spectra. This indicates that the four alkene stretches arise from chemisorbed rather than physisorbed layers, since physisorbed layers would be expected to desorb at elevated temperatures. Annealing to 560 K, however, produces noticeable changes in the C−H stretching region as well as a concurrent increase in the Si−H absorbance. These correlated changes indicate that the changes in the C−H stretching region upon annealing to 560 K arise from dissociation rather than simple rearrangement of the molecular conformations.

Figure 7 shows the results of exposing a single-domain Si-(001) surface to 1,3-CHD at 120 and 300 K and, for comparison, the spectrum of an ice of 1,3-CHD. The bottom two spectra were taken using s-polarized light with the electric field along the $\langle 1\bar{1}0 \rangle$ direction, perpendicular to the Si=Si dimer axis. The bottom spectrum was obtained after exposure of Si(001) to 1 Langmuir with the sample at a temperature of 120 K, while the middle spectrum was obtained after exposure of Si(001) to 5 Langmuirs at a temperature of 300 K; both spectra were acquired at the dosing temperature. The top spectrum was obtained by exposing a sample at 100 K to 10 Langmuirs of 1,3-CHD; under these conditions 1,3-CHD freezes into a multilayer ice on the sample. Since the spectrum taken after adsorption of 1 Langmuir of 1,3-CHD at 120 K does not resemble the ice spectrum, we can be confident that this spectrum is probing a chemisorbed layer of 1,3-CHD and not a physisorbed one. It is interesting then to note that the bottom two spectra are similar in appearance.

For 1,3-CHD on Si(001), our STM images reveal at least three different bonding configurations, differing in their bonding symmetry with respect to the underlying Si=Si dimers. FTIR reveals an unusually broad absorbance in the alkene C−H stretching region with at least four peaks detectable. The assignment of bonding configurations from the FTIR data alone is complicated by the fact that each bonding geometry has a H−C=C−H (alkene) group. If the adsorbed molecules have a
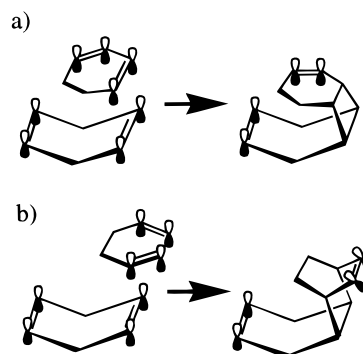

Figure 8. Schematic illustration of the interaction of 1,3-cyclohexadiene with the Si(001) surface. (a) [2 + 2] interaction of one 1,3-cyclohexadiene C=C bond with a Si=Si dimer. (b) [4 + 2] interaction of both 1,3-cyclohexadiene C=C bonds with a Si=Si dimer.

local C_{2v} site symmetry, then each molecule will give rise to two alkene C−H vibrations separated by approximately 10 cm^{-1}. Experimentally, our FTIR spectra show at least four distinguishable peaks in the alkene stretching region. The observation of more than two peaks demonstrates that either the molecules are adsorbed into a low-symmetry site or they are adsorbed in two different configurations. Our STM data clearly shows at least two types of surface species at different locations, favoring the latter interpretation. Figure 8 schematically depicts the bonding configurations produced by the [2 + 2] (Figure 8a) and [4 + 2] (Figure 8b) reactions. The A-type protrusions have their center located approximately above a dimer; the best fit for these protrusions is the product formed from the reaction of both C=C bonds with the surface, as depicted in Figure 8b. The C-type protrusions appear asymmetric with respect to the dimer; the best fit for these protrusions is the product formed from the reaction of one C=C bond with the surface, as depicted in Figure 8a. The B-type protrusions (which only account for approximately 10% of the adsorbed molecules) are perhaps the result of a third reaction, possibly one that results in some dissociation. Thus, for 1,3-CHD we find that approximately 55% of the molecule interacts via a [4 + 2] process, 35% via a [2 + 2] process, and approximately 10% produces an unknown surface structure which might be related to molecular dissociation processes or defects on the surface.

Discussion

Our results show several important facts. First, we find that for 1,3-dienes the [4 + 2] product is preferred but that the [2 + 2] product occurs with relatively high probability, so that there is little selectivity in the reactions of these dienes with the Si-(001) surface. Furthermore, heating the surface does not lead to a transition to the [4 + 2] product but instead leads to dissociation. One important consequence of this inability to obtain a unique bonding configuration for 1,3-dienes on the Si-(001) surface is that monolayer films produced by [4 + 2] processes are likely to show a higher degree of structural disorder than those produced by the corresponding [2 + 2] reactions of simple alkenes containing only one unsaturated bond. Indeed, our STM studies of 1,3-dienes have failed to show any ordered structures produced at higher coverage; we believe this is a direct result of the chemical disorder of the surface adsorbates.

The present results, combined with the results of our previous work with unsaturated cyclic nonconjugated alkenes, have raised a number of questions. One question is what makes the reactions of alkenes with the Si(001) surface so facile? This is
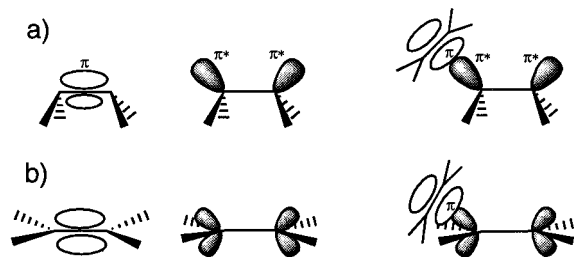
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Figure 9. Schematic illustration of the spatial distribution of the π bonding and π^* antibonding orbitals for Si=Si in (a) bent and (b) planar configurations. A schematic depiction of the filled π-bonding orbital of an alkene interacting with the empty π^* antibonding orbital of the Si=Si dimer is shown for each geometry. Note that interaction is unobstructed for the bent Si=Si dimer configuration at the top but is sterically hindered for the planar configuration at the bottom.

especially intriguing because the analogous [2 + 2] cycloaddition reactions of organic species are highly forbidden by symmetry considerations. A related question is why is the selectivity of the surface reactions between Si(001) and the 1,3-dienes comparatively poor?

To answer these questions, we note that the Si=Si dimers have three differences from their alkene analogs. First, the substitution of Si for C; second, the bending out of a planar configuration; third, the dynamic tilting and resulting zwitterionic character. The reaction of two organic alkenes via a [2 + 2] reaction is formally forbidden because the high-symmetry interaction of two alkenes in their ground electronic states correlates with an excited electronic state of the final product.[20,21] This leads to a very large activation barrier for reaction in the high-symmetry configuration. A second mode of interaction known as a "suprafacial−antarafacial" interaction is allowed but is sterically very hindered; indeed, we have shown previously using infrared spectroscopy of isotopically labeled ethylene that the stereochemistry of the addition product is inconsistent with the suprafacial−antarafacial bonding mechanism.[34] A previous theoretical study of acetylene adsorption on the Si(001) surface proposed that ethylene adsorption was facile because the adsorption can proceed through a three-membered ring formed by one Si atom and the two carbon atoms of the alkene unit.[35] We have repeated these calculations at the Hartree−Fock level for ethylene on Si(001) at the 3-21+G* level using the Gaussian94 program[36] and also found that this mode of adsorption has no barrier while the high-symmetry interaction has a barrier of several electronvolts. Thus, we believe that the formation of a three-membered ring is likely central to the facile manner in which alkenes bond to the Si-(001) surface.

We propose that the possibility of forming such a three-membered ring is the critical factor determining why alkene reactions on Si(001) are so facile while the analogous [2 + 2] reactions between two alkenes as well as the reaction between alkenes and disilenes are extremely slow. As depicted in Figure 9, the formation of a π bond between the two Si atoms in a Si=Si dimer results in increased electron density in the central region between the two Si atoms and in a depletion of electron density at the edges of the dimers at the location of the π^*-antibonding state; indeed, STM images of the unoccupied electronic states of Si(001) clearly show that the π^*-antibonding state is localized at the ends of the dimers.[4] The alkenes, in contrast, have a high electron density; thus, the formation of a three-membered ring can be viewed as a simple electrostatic interaction between the electron-deficient end of a Si=Si dimer and the electron-rich π bond of the alkene. If this situation is compared with typical typical organic [2 + 2] reactions or even

the reaction of an alkene with a typical disilene, one finds that the critical difference is that on the Si(001) surface the dimers are bent out of a planar configuration. Whereas for typical alkenes or disilenes this positively charged region (correponding to the π^*-antibonding state) is present, it is sterically hindered by the planar geometry. In contrast, the Si=Si dimers are significantly bent from their planar configuration, making the π^* region physically accessible for interaction with the C=C bond of an incident alkene, leading to facile reaction. The picture is supported by studies of the reactions of disilenes with alkenes and alkynes; here, it has been observed that [2 + 2] reactions can occur, but they do so slowly and with loss of stereochemistry, suggesting a diradial mechanism.[22,23,37]

We now compare the [4 + 2] reaction with the [2 + 2] reaction. A previous theoretical study of 1,3-CHD bonding with Si(001) predicted the enthalpy change in forming the [4 + 2] product from Si(001)−(2 × 1) and gas-phase 1,3-CHD to be 54.0 kcal/mol, while the enthalpy change for the [2 + 2] reaction was predicted to be only 38.8 kcal/mol.[24] Thus, the product of the [4 + 2] reaction is predicted to be 15.2 kcal/mol more stable than the product of the [2 + 2] reaction. This result also makes intuitive sense since the [4 + 2] reaction produces a six-membered Si_2C_4 ring at the interface while the [2 + 2] reaction produces a strained four-membered Si_2C_2 ring at the interface. The 15.2 kcal/mol energy difference is sufficiently large that one would not expect to see significant amounts of the [2 + 2] product if the product distribution was thermodynamically controlled. However, our experimental data for both DMBD and CHD shows the formation of significant quantities of both products. Specifically, our data shows that for DMBD, 80% of the molecules bond to the surface through a [4 + 2] process and 20% bond via a [2 + 2] type reaction, while for 1,3-CHD, 55% bond via a [4 + 2] process, 35% via a [2 + 2] process, and the remainder though an unknown process. The important conclusion that can be drawn from the observation of significant amounts of a thermodynamically unfavorable product is that thermodynamics are probably not the primary driving force behind the reactions.

The possible effect of thermodynamics on the reaction probabilities can be further examined by varying the dosing temperature. The spectra in Figure 7 for 1,3-CHD show that adsorption onto a 120 K surface yields an infrared spectrum nearly identical to that obtained by adsorption onto a 300 K surface. Since the thermodynamic stabilities of these species are theoretically predicted to be significantly different, the absence of any significant temperature dependence suggests that the product distributions are controlled by the reaction kinetics rather than the thermodynamics. We, furthermore, note that, in principle, it should be possible to allow the system to come to thermodynamic equilibrium by providing sufficient thermal energy to allow the system to explore the complete phase space of available bonding configurations. Yet, we find that thermal annealing does not change the product distributions but instead leads to fragmentation. Since a change from one bonding geometry to another requires cleavage of at least one of the Si−C bonds, this process is likely to have a very high activation barrier. Indeed, our results suggest that cleavage of C−H bonds occurs more readily, leading to molecular dissociation that is evident from the appearance of Si−H stretching vibrations in the FTIR spectra.

Conclusions

While many details of the interaction of alkenes with Si-(001) surfaces remain unknown, it is clear that the [4 + 2]

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reaction, while it may form a more thermodynamically favored product, is not the only product. Although the end product is higher in energy, the [2 + 2] reaction is also quite facile. Moreover, the likely high activation barrier from one product to the other appears to preclude achieving a single reaction product by thermal annealing. It is possible, however, that improved selectivity could be achieved by making use of steric control. In the case of DMBD, for example, part of the improved selectivity for the [4 + 2] process might well arise from the bulky nature of the methyl groups, which might hinder the [2 + 2] process.

Finally, we can summarize by making the general observation that the formation of [2 + 2] products as well as [4 + 2] products when 1,3-dienes adsorb on the Si(001)-2 × 1 surface has important consequences for the possible formation of highly ordered organic films on Si(001). While we have shown previously the ability to form highly ordered films of simple alkenes and nonconjugated dienes via [2 + 2] processes, achieving similar order via [4 + 2] processes from 1,3-dienes will be difficult and likely would require very careful use of steric hindrance and/or electronic structure effects. Overall, we conclude that while the [4 + 2] reaction creates a less strained interface, the [2 + 2] is likely a more favorable reaction for the creation of highly ordered organic layers.

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