

DFT Investigation of Product Distribution Following Reaction of 1,3-Cyclohexadiene on the Si(100)-2×1 Surface

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Density functional theory (DFT) was used to study different possible bonding geometries of 1,3-cyclohexadiene (1,3-CHD) on the Si(100)-2×1 surface and for comparison with recent STM experiments. Full geometry-optimized structures were obtained for all adducts, including intra- and interdimer reaction products. These results were analyzed both in terms of the total energy values and the detailed optimized geometries. Comparison with the product distribution observed by STM demonstrates that the reaction is kinetically controlled. However, the inability to explain the observed product distribution within the framework of the present total energy calculations and earlier cluster calculations of the transition state indicates that there are serious gaps in our understanding of the reaction dynamics of 1,3-CHD on Si(100).

Introduction

The ever-increasing demand for smaller and faster devices has led to a growing interest in the potential use of molecules in device applications. Of particular interest is the ability to integrate organic molecules and molecular thin films into existing Si-based technologies. The prospects for integration have dramatically improved following recent experimental observations that demonstrate small organics can attach to Si-(100) surfaces via the Si–Si dimer bond.^{1–9} The Si–Si dimer bonds offer several possible modes of attachment. The existence of both σ and weak π bonds between the Si dimer atoms opens up the possibility of reactions that exploit the presence of unsaturated Si double bonds on the surface. However, the Si dimer is also known to tilt back and forth in an anticorrelated fashion with neighboring dimers, on a characteristic time scale on the order of 1 ps at room temperature. Tilting eliminates the degenerate ground state, such that the local hybridization on the upper atom of the dimer is sp^3 -like, while that on the lower atom is largely sp^2 . Tilting is thus accompanied by charge transfer from the lower atom, which has a dangling bond with significant p character, to the upper atom of the dimer, which has significant s character. Dimer tilting therefore opens up the possibility of zwitterionic type reactions, that is, reactions in which the upper dimer atom acts as a nucleophile, while the lower atom is an electrophile. However, regardless of type of reaction involved, if organics are to prove feasible as molecular building blocks on Si(100), it is essential to establish a detailed understanding of the reaction mechanisms and the factors that control attachment geometry.

Here in this present work, we focus on cycloaddition reactions involving the Si(100) dimer units and the π system of the organic molecule. In particular, we will focus on reactions involving 1,3-cyclohexadiene (1,3-CHD), which is in principle

capable of undergoing both [4+2] and [2+2] cycloaddition reactions, the latter being formally forbidden on the basis of the Woodward–Hoffmann orbital symmetry rules. Earlier theoretical studies of this system predicted that formation of the [4+2] product is favored and that there is no significant barrier to reaction.^{10,11} Experimental studies including STM,² MIR–FTIR, and NEXAFS¹² provided evidence for intradimer [4+2] and [2+2] reaction products. On the basis of these early STM and MIR–FTIR studies, the intradimer [4+2] or Diels–Alder product was identified as the dominant product. However, the aforementioned theoretical and experimental studies considered [4+2] and [2+2] reactions that involved only *single* Si dimer units. Interdimer and inter-row reactions were not considered. Our recent STM studies¹ indicate that cycloaddition of 1,3-CHD to the Si(100) surface includes, but is not limited to, reaction with single Si dimers. We showed that two types of interdimer reactions occur, that is, reactions involving two adjacent Si dimers within the same row or neighboring dimers in adjacent rows. The identification of these interdimer reaction products and their distribution on the surface provided direct evidence that the reaction is kinetically controlled. In the present study, we use DFT methods to analyze the total energy and optimized structures of the different possible reaction products, including products that are energetically favorable but never observed by STM.

Computational Details

DFT slab calculations were performed using Cambridge Serial Total Energy Package (CASTEP).¹³ Each slab was six Si layers deep, with the bottom two layers fixed at their bulk positions, while the top four Si layers and the 1,3-CHD molecule were not fixed and allowed to fully relax. Hydrogen was used to terminate the dangling bonds on the bottom layer of the slab and was also fixed. Cells were repeated in *x*, *y*, and *z* directions with a vacuum separation between slabs of ~ 10 Å along the *z* direction. For single dimer reactions, each cell was three Si

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TABLE 1. Relative Total Energy Values for Geometry Optimized Structures^a

product	ΔE	ΔE (corrected)	population (%)
[4+2] intradimer (A)	0	0	11
[4+2] interdimer (C)	+5.3 kcal/mol	-3.2 kcal/mol	31
[4+2] interdimer (same row; reversed)	+5.5 kcal/mol	-3.0 kcal/mol	0
[4+2] inter-row (B)	+15.8 kcal/mol	+2.0 kcal/mol	16
[2+2] intradimer (D)	+16.2 kcal/mol	+16.2 kcal/mol	10
[2+2] interdimer (E)	+23.5 kcal/mol	+15.0 kcal/mol	12

^a The corrected energies take account of the presence of surface-dangling bonds and the correction factor is 8.5 and 13.8 kcal/mol for the interdimer and inter-row products, respectively.

dimers in length and one dimer row wide (i.e., a 2×3 cell) with the middle dimer of the row reacted with a 1,3-CHD molecule. A single bare dimer remained on either side of the reaction site within the supercell, thus each reaction site is separated by two bare dimers when periodic boundary conditions are applied. Total energy optimizations involving cells two dimers wide and two dimers in length (4×2 cells) were performed for both the [4+2] intradimer product and the [4+2] inter-row product. Additional total energy calculations involving the [4+2] intradimer product in a 4×2 cell were performed to allow a direct comparison of the energies of the inter-row and interdimer products.

The calculations utilized the PW91 generalized gradient approximation (GGA) functional with Perdew–Zunger parametrization¹⁴ for the electron exchange–correlation interaction. Ultrasoft pseudopotentials were used for Si, C, and H atoms. The energy cutoff for the plane wave expansion was 230 eV. The Monkhorst–Pack^{15,16} scheme was used for k -point sampling in which meshes equivalent to 2×3 were used ($1 \times 1 \times 3$ for 4×2 dimer cells). The tolerance for RMS displacement on atoms was 0.001 Å while the tolerance for RMS force on atoms was 0.05 eV/Å. The total energy convergence criterion was 0.2×10^{-4} eV/atom, or better than 0.1 kcal/mol for the larger cell described above. The accuracy of the total energy values reported here is expected to be significantly better than 1 kcal/mol.

Results and Discussion

Table 1 details the calculated total energy values for each of the optimized geometries together with the experimentally observed populations determined by STM. The results of these calculations demonstrate that the [4+2] intradimer product has the lowest total energy, so that all energies reported in Table 1 are referenced to the [4+2] thermodynamic product. In particular, the [4+2] intradimer product is favored over the intradimer and interdimer [2+2], which have energies of +16.2 and 23.5 kcal/mol, respectively. The results of our slab calculations are in general agreement with previous cluster calculations of the [2+2] intradimer product by Konecny and Doren¹⁰ who reported a value of 15.2 kcal/mol but somewhat lower than the values of 21.7 and 21.8 kcal/mol reported by and Choi and Gordon.¹¹ The two values reported by Choi and Gordon¹¹ reflect the energy of the two possible [2+2] conformers. In each case, the increased energy associated with [2+2] products¹ can be attributed to significant ring strain in the adduct, in agreement with the conclusions of Konecny and Doren.¹⁰ Figure 1 details the results of our geometry optimized slab calculations. The intradimer [2+2] product is attached via a four-membered ring with bond angles of 80.8° and 77.1°. These bond angles together with the elongated C–C bond in the four-member ring (1.56 Å) are indicative of significant ring strain.

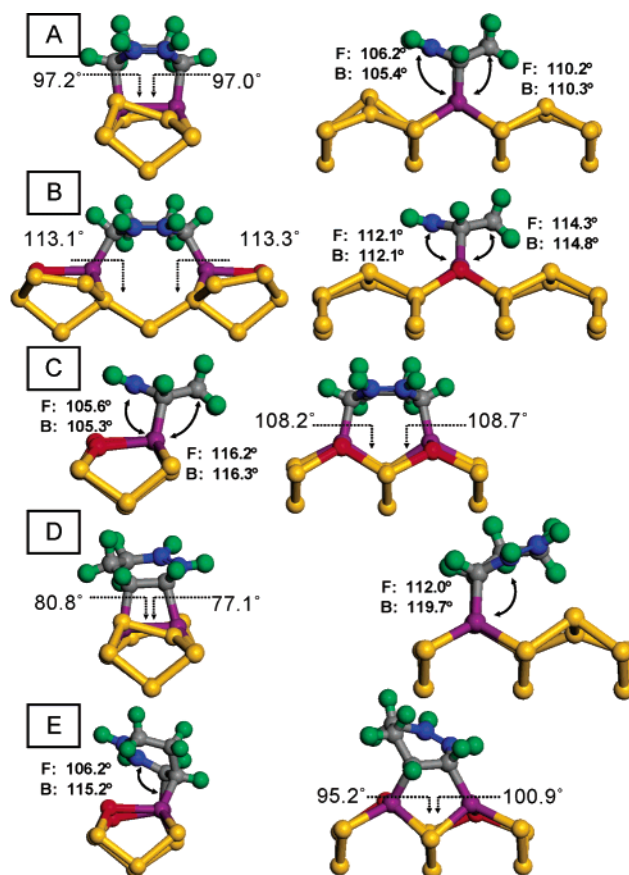


Figure 1. Optimized structures for 1,3-CHD on Si(100). (A–E) show ball-and-stick models for the five reaction products of 1,3-CHD found on the Si(100) surface. The different reaction products are as follows: (A) [4+2] intradimer, (B) [4+2] interdimer across rows, (C) [4+2] interdimer same row, (D) [2+2] intradimer, and (E) [2+2] interdimer. Si atoms are shown in yellow, carbon shown in gray, and hydrogen in green. The single remaining C=C is indicated in blue. Si–C bonds are indicated in purple, and Si atoms with dangling bonds are indicated in red. C–Si–Si and C–C–Si bond angles are also indicated. The latter are designated as being either in the front (F) or back (B) of the molecule with respect to the view provided in the figure.

The interdimer [2+2] product, on the other hand, is attached via a five-member ring. Although the bond angles of 95.2° and 100.9° are indicative of reduced ring strain, the interdimer product is highest in energy because of the presence of a single dangling bond (red Si atoms shown in Figure 1) at each of the two reacted dimers.

To estimate the energy of these dangling bonds, we studied three additional cells each four Si(100) dimers in length and containing six surface hydrogen atoms and two dangling bonds. One cell was π -bonded with both dangling bonds on the same dimer, while the others had dangling bonds on the same and opposite sides of adjacent dimers. Relative to the π -bonded paired configuration, the cells with dangling bonds on the same and opposite side of the dimer were higher in energy by 8.5 and 13.8 kcal/mol, respectively. These results are in good agreement with values of 7–13 kcal/mol¹⁷ reported for the pairing energies of dangling bonds on Si(100). Thus, there is an additional energy cost of about 8.5 kcal/mol corresponding to the dangling bonds associated with the [2+2] interdimer product and this is included in the total energy value of 23.5 kcal/mol in Table 1. A corrected value of the total energy (see Table 1) is obtained by eliminating the energy cost of these dangling bonds. The corrected energy value better reflects the binding energy of the reaction product, including the strain

energy in the molecular adduct. The correction factor in the inter-row products is even higher, 13.8 kcal/mol, because of the lack of any coupling between the dangling bonds. In this manner, we can estimate that the ring strain in the [2+2] intradimer products is about 1 kcal/mol higher than that in the interdimer [2+2] product. This trend is consistent with the behavior observed in cyclic aliphatic hydrocarbons where the strain in four-member ring systems can be as much as 18 kcal/mol higher than that observed in five-member rings.¹⁸ The significantly reduced difference in ring strain is likely a result of the fact that the rings are comprised of longer and more weakly bound Si–Si and Si–C bonds.

Table 1 also shows the total relative energies and corrected energies for the [4+2] products. Allowing for the dangling bond contribution to the total energy, and the similar [4+2] attachment motif, the ring strain in the interdimer product can be estimated to be at least 3 kcal/mol lower than the thermodynamically favored intradimer product (see Table 1). The difference in ring structures is once again evident from the optimized geometries shown in Figure 1. The intradimer product is attached to both atoms of a Si dimer unit via a six-member ring. However, because the Si–Si dimer bond (2.35 Å) is dramatically longer than either the C–C single (1.54 Å) or double (1.34 Å) bonds, the ring is forced to expand resulting in C–Si–Si bond angles of 97.2° and 97°. In contrast, the interdimer [4+2] product is attached via a seven-member ring formed with adjacent dimers in the same row (see Figure 1). The seven-member ring is more relaxed with bond angles of 108.2° and 108.7° and significantly closer to the ideal tetrahedral bonding geometry. On the other hand, the inter-row [4+2] product involves reaction between adjacent dimers in adjacent rows and attaches to the surface via a strained nine-member ring with bond angles of 113°. After correcting for the dangling bond energy, the inter-row product (nine-member ring) is approximately 5 kcal/mol less stable than the kinetic interdimer product (seven-member ring) and 2 kcal/mol less stable than the thermodynamic intradimer product (strained six-membered ring). This trend is qualitatively consistent with the behavior of cyclic hydrocarbons where an increased ring strain is observed for ring sizes that are smaller and larger than the optimized strain-free ring structure.

The results of these total energy calculations do little to shed light on the factors that control the product distribution. In particular, the [4+2] intradimer product, which is thermodynamically preferred by over 5 kcal/mol, has a surface population of only 11%, whereas higher total energy but kinetically preferred [4+2] interdimer product (same row), has a population of 31%. Transition-state searches performed by Konecny and Doren¹⁰ and Choi and Gordon¹¹ both indicate that there is essentially no energy barrier to the formation of the [4+2] intradimer product. On this basis, one might expect that no significant distortion of the molecule or surface is required for reaction, that is, reaction involves an early or reactant-like transition state, which is consistent with the large calculated exothermicity (54 kcal/mol). However, when expressed in terms of an energy barrier, the 3-fold difference in population between the intradimer and interdimer [4+2] products (see Table 1) following reaction at 300 K can be accounted for by an energy barrier difference of only 0.7 kcal/mol, which is well within the errors bars of any transition-state calculation. It is important to recognize that no attempt was made to measure the actual sticking coefficient during our experiments, so that only relative values can be inferred on the basis of the product distribution. Also, the transition-state calculations described above were performed only for the [4+2] and [2+2] intradimer products,

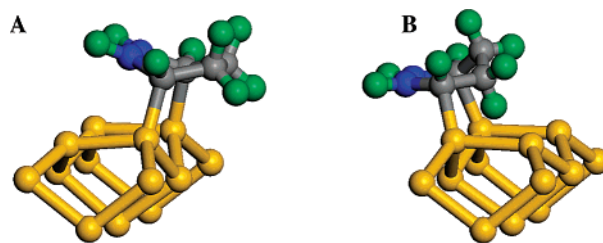


Figure 2. Possible forms of the kinetically favored [4+2] interdimer product. A and B are ball-and-stick models of the two possible forms of the [4+2] interdimer product of 1,3-CHD with neighboring dimers in the same row. A is the experimentally observed product and B is unobserved in STM images. Si atoms are indicated in yellow, C are gray, H are green, and the C=C bond is indicated in blue. Calculations indicated that product B is lower in energy by 0.2 kcal/mol.

the latter having a barrier of 5.9–8 kcal/mol. So if indeed there is a barrier for the [4+2] interdimer product, it would necessarily have to be smaller than the [4+2] intradimer (which is calculated to be barrierless) to be consistent with the observed populations. This is surprising since in contrast to the intradimer reaction, which is symmetry allowed and likely a concerted pericyclic-like process, the interdimer reaction involves breaking two Si dimer π bonds and generates two weakly coupled dangling bonds or radicals, with an energy cost of 8.5 kcal/mol.

If there is in fact no energetic barrier to formation of the [4+2] intradimer product and perhaps even the [4+2] interdimer product, the product distribution must then be controlled by the entropy of the transition state and the collision dynamics of 1,3-CHD molecules on the surface or possibly the degeneracy of reactive surface sites. The latter, however, is unlikely to be a significant factor for the low coverage conditions discussed here since the number of available sites is essentially the same for all [4+2] products. The dominant factor must then be the entropy of the transition state and the manner in which the molecule has to approach the surface dimers for reaction to take place. In principle, it is possible that the energy barrier for the intra- and interdimer products are both negligible but that the transition state for the interdimer reaction is less constrained and thus has a lower free energy. The optimized geometries in Figure 1 provide some evidence to support this view. Since the bond angles in the interdimer [4+2] product are closest to those found in the free 1,3-CHD molecule, it is likely that less reorientation and reorganization of the molecule is required for reaction. However, one cannot push these arguments too far since if there is any activation energy required for molecules to adopt the best configuration for reaction, then this should show up both in the energy and the free energy.

Although we have not measured actual sticking coefficients, on the basis of the gas exposure and the observed surface concentration we can estimate that at low coverages at least 50% of incident molecules react with the Si(100) surface. However, despite the strong driving force for product formation it would be incorrect to suggest that the reaction is unselective and the product distribution simply reflects statistical collision encounters with the surface. This becomes strikingly apparent when it is realized that there is one particular product that is missing from the surface population. There are two possible forms of the kinetically favored [4+2] interdimer (same row) product (Figure 2). One has the remaining double bond in the reacted molecule positioned in the middle of the dimer row, whereas the other product has the double bond above the trench between dimer rows. The former product is the only one that is observed and is indeed the dominant kinetic product. However, total energy calculations (Table 1) reveal that the observed

product is the higher-energy isomer, the energy difference being attributed to the steric interaction between the overhanging molecular adduct and the dimer rows, and which is absent when the molecule hangs over the trench site. Clearly, there must exist specific interactions in the transition state that favor the kinetic product but preclude formation of the lower energy interdimer product.

Conclusions

Density functional theory (DFT) was used to study different possible bonding geometries of 1,3-cyclohexadiene (1,3-CHD) on the Si(100)-2×1 surface and to compare these results with recent STM experiments¹. Full geometry optimized structures were obtained for all adducts, including intra- and interdimer reaction products. These results were analyzed both in terms of the total energy values and the detailed optimized geometries. The total energies of the molecule adducts themselves were estimated by correcting the total calculated energy for the presence of dangling bonds in the products. Comparison with the product distribution observed by STM demonstrates clearly that the reaction is kinetically controlled. In agreement with earlier calculations, we find that the [4+2] products are energetically favored over the [2+2] products, largely because of ring strain. Of the [4+2] products, the intradimer product is energetically favored, but when allowance is made for the dangling bond energy, the interdimer and inter-row products straddle the energy of the intradimer product, being about 3 kcal/mol lower and higher, respectively, an energy ordering that can also be rationalized on the basis of ring strain.

The biggest remaining controversy concerning the reaction of 1,3-CHD on Si(100) centers about the origin of the observed surface population. The kinetic product is the interdimer [4+2] product but there are significant populations of other inter-row [4+2] and even intradimer and interdimer [2+2] products. These observations are inconsistent with prior transition-state calculations that predicted an absence of any appreciable barrier to

formation of the intradimer [4+2] product and a significant barrier for the [2+2] reaction. The barriers that exist and whether there are dynamical bottlenecks associated with specific molecular or surface geometries required for reaction remain to be established. However, it is clear that even though the reactivity of 1,3-CHD is high, the reaction is not indiscriminate since products that should be accessible are explicitly excluded from the surface population.

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