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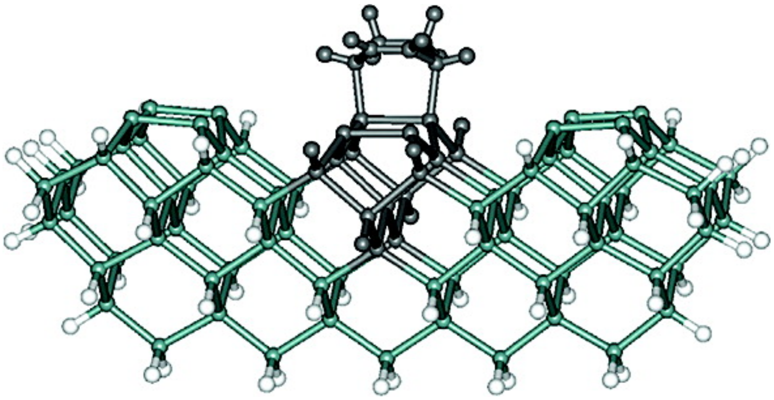

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Cycloaddition Isomerizations of Adsorbed 1,3-Cyclohexadiene on Si(100)-2×1 Surface: First Neighbor Interactions

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Abstract: The initial and subsequent surface reaction mechanisms of 1,3-cyclohexadiene on the Si(100)-2×1 surface were theoretically explored, focusing on the possible first-neighbor interactions. Five different initial reaction channels leading to nine different surface products were identified, confirming previous experimental reports of inter-dimer structures. Among the nine identified products, five of these surface products are new species that have not previously been reported. Potential energy surface studies reveal that the net reaction barriers within a given channel are very small, indicating that the final product distributions within that channel are determined by thermodynamics. On the other hand, thermal isomerizations between different channels are not expected to occur easily. Therefore, the surface product distributions among the five different channels are more likely to be determined by kinetics. As a result, understanding the relationships among the available reaction channels both kinetically and thermodynamically is essential for properly interpreting the experimental results. The current study shows that the subsequent surface chemical reactions of unsaturated initial surface products are strongly coupled with the first-neighbor interactions.

I. Introduction

With advances in experimental techniques, increasing effort is being directed to the development of synthetically modified semiconductor surfaces.[1] Many saturated and unsaturated organic and organometallic compounds are actively being tested for the creation of new interfacial chemical bonds that would potentially add new functionalities to semiconductor technology. Due to the limited resolution of experimental techniques, however, it is becoming apparent that the interplay between experimental and theoretical studies is crucial to better understand complex surface reactions.

Surface reactions of unsaturated organic compounds with the Si(100)-2×1 reconstructed surface have been good examples for both theory and experiment. Reactions of alkynes and alkenes with the Si(100)-2×1 surface resemble formally orbital symmetry-forbidden[2] $[2_s+2_s]$ cycloadditions. Thus, a large reaction barrier is expected along the symmetric reaction pathway. In fact, it is known from carbon solution chemistry that even the low symmetry reaction pathway has a high reaction barrier, mainly due to unfavorable geometric configurations along the reaction path.[3] However, the rules governing [2+2] additions on Si surfaces are apparently different, since many instances of formally forbidden reactions have been reported. Early experimental[4] and theoretical[5] studies have shown that ethylene, propylene, and acetylene easily chemisorb on the Si(100)-2×1 surface, yielding [2+2] products, and are able to resist temperatures of up to 600 K.

Theoretically, Liu and Hoffmann[5b] have found a low symmetry pathway of the acetylene adsorption on the Si(100) surface that involves a π-complex precursor and a biradical intermediate that has a low energy barrier to [2+2] cycloaddition products, substantiating the experimental findings. Recent experimental[6] and theoretical[7] studies identified other possible surface products of acetylene, adding a new complexity to the surface reactions of ene systems.

Diene systems have also been actively studied. For example, for 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, theoretical and experimental studies have shown[8] that the surface dimer can

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act as a good dienophile yielding “Diels−Alder”-like [4+2] cycloaddition products, in which a conjugated diene reacts with the silicon surface dimer to form a six-membered ring.

Reinvestigation of the 2,3-dimethyl-1,3-butadiene reaction on the Si(100)-2×1 surface by Hamers and co-workers[9] support the observation that the Diels−Alder product represents 80% of the surface products. However, they noted a minor (20%) [2+2] product as well. In the case of 1,3-cyclohexadiene, they observed 55% of the [4+2] products, 35% of the [2+2] product, and 10% unknown, strongly indicating the existence of competition between [4+2] and [2+2] reactions of the diene on the Si(100) surface. Attempts to convert the product distribution to the thermodynamically more stable product by annealing to higher temperatures failed. Subsequent theoretical studies[10] provided further support for the existence of competing reactions by showing that there exists a low energy [2+2] cycloaddition pathway on the Si(100) surface and that surface isomerization reactions connecting [4+2] and [2+2] products are very unlikely due to a high activation barrier.

These new experimental and theoretical studies indicate that the final surface reaction products are determined during the initial stage of the surface reactions and that they are not subject to further thermal redistributions or isomerizations among surface products. This provides very strong evidence that the control of the surface selectivity toward a diene is determined by the reaction kinetics rather than by the thermodynamics.

Minary and Tuckerman[11] recently considered the dynamic aspects of the cycloaddition reactions of 1,3-butadiene on the Si(100)-2×1 surface with ab-initio molecular dynamics. They showed that a stepwise zwitterionic mechanism governs the addition product formation.

Surface structures with interfacial bonding involving more than one surface Si dimer also have been reported. For 1,3,5,7-cyclooctatetraene on the Si(100) surface, Hovis and Hamers[12] showed that first-neighbor interactions along the dimer-row are possible via a double [2+2] cycloaddition reaction between two C=C groups and two Si=Si surface dimers. Recently, Teague and Boland,[13] in addition to the previously observed intra-dimer (or on-dimer) [2+2] and [4+2] products of 1,3-cyclohexadiene on the Si(100) surface, identified two different intra-dimer [2+2] conformers and two different inter-dimer [4+2] products (see Figure 1). The two different [2+2] intra-dimer conformers, differing in the conformations of the two sp^3 carbons of the adsorbed 1,3-cyclohexadiene, were assigned as the two experimentally observed species in a previous work by the present authors.[10a] According to the recent experimental results reported by Teague and Boland,[12] the inter-dimer [4+2] product involving neighboring dimers in the same row, **1c**, is the dominant surface product, despite the presence of unpaired dangling bonds on two adjacent dimers. They also suggested an alternative inter-dimer species, **1d**, in which the two carbon atoms are attached to two adjacent dimers across two rows.

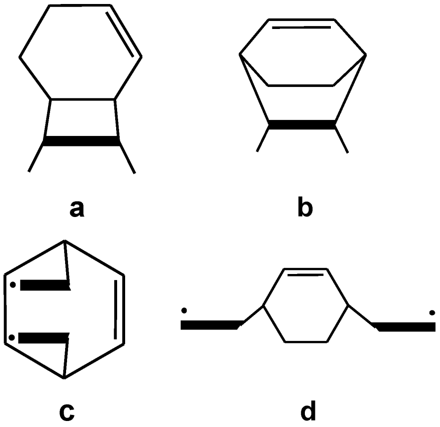

Figure 1. Previously identified and suggested initial surface products of 1,3-cyclohexadiene on the Si(100) surface. The thick line represents the surface Si dimer. (a) Intra-[2+2] product. (b) Intra-[4+2] product. (c) Inter-[4+2] product in the same row. (d) Inter-[4+2] product across the row.

These studies imply either that the initially formed intra-dimer [2+2] and [4+2] products (see Figure 1a and 1b) can undergo subsequent surface isomerizations (perhaps due to residual π-bonding) and/or that there are other entrance channels in addition to those already identified for surface cycloadditions. Understanding the possibility of residual π-bonding in the initially formed adsorbed species is very important, since this can provide a surface environment that is conducive to secondary surface adsorption. If, on the other hand, the residual π-character in the initially adsorbed species is used for surface isomerizations, the surface may become less reactive. If this happens, subsequent surface adsorptions may be retarded. Furthermore, the possibilities of additional initial reaction channels can lead to new insights regarding surface characteristics.

It is therefore of interest to explore the interactions of adsorbing species with multiple surface dimers. In this paper, an extensive theoretical study of the potential energy surface describing the reaction mechanisms is presented in which both possible secondary surface isomerizations and new initial reaction channels involving multiple surface dimers are explored.

The [4+2] reaction along and across the Si dimer-row create unique surface diradicals as shown in **1c** and **1d**, respectively. The diradicals shall be emphasized by representing them as **R**.

II. Computational Details

The all-electron 6-31G(d)[14] basis set was used as the primary basis set in this work. Minimum energy reaction paths were determined by first optimizing the geometries of the minima and transition states. Then, each stationary point was characterized by computing and diagonalizing the Hessian matrix (matrix of energy second derivatives). To follow the minimum energy path (MEP), the Gonzalez−Schlegel second-order method[15] was used with a step size of 0.3 amu$^{1/2}$ bohr.

Various points on the reaction paths, particularly transition states and intermediates, are often inherently multiconfigurational. Therefore, CASSCF (complete active space SCF)[16] wave functions were primarily used to describe these species. For the study of reaction paths leading

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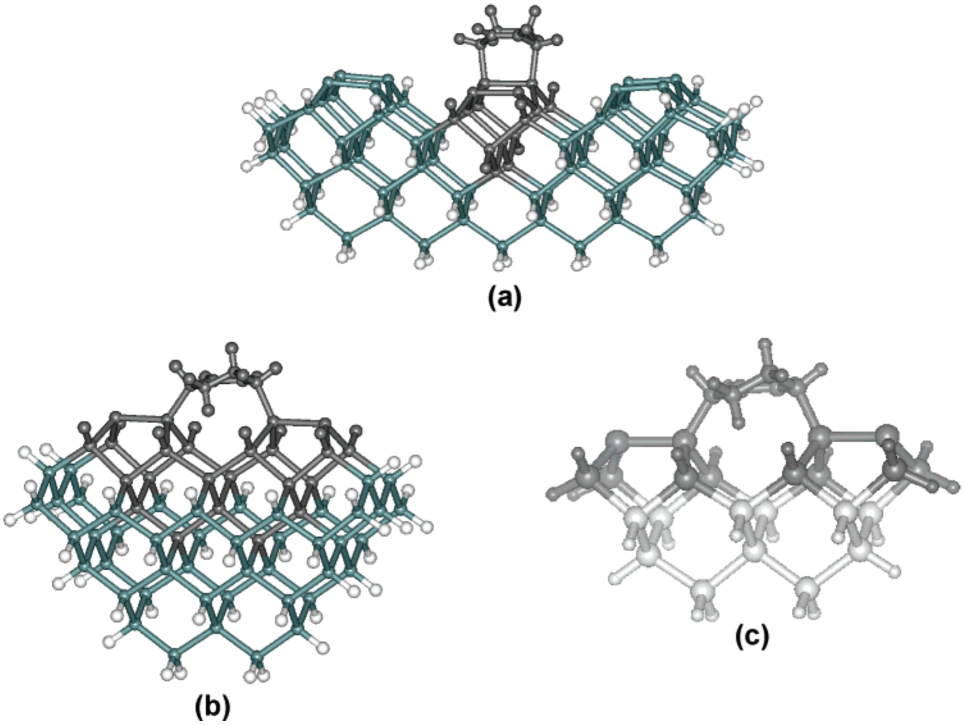

Figure 2. Two different SIMOMM models used in this study. (a) For the along the dimer-row products, a $C_6H_{24}Si_{15}$ quantum region is embedded in a $C_6H_{68}Si_{80}$ cluster. (b) For the across the dimer-row products, a $C_6H_{32}Si_{23}$ quantum region is embedded in a $C_6H_{60}Si_{60}$ cluster. (c) 6-31G(d) and 3-21G basis sets were used for the most active part ($C_6H_{22}Si_{12}$) and the less active part ($Si_{11}H_{10}$) of the quantum region of 2b model, respectively. The corresponding two basis set regions are shown in darker and lighter gray colors.

to products, an (8,8) active space was used. This active space is constructed from the four electrons in the two sets of π- and π^*-orbitals of 1,3-cyclohexadiene, plus the four electrons and π- and π^*-orbitals of the two surface Si dimers.

To recover the dynamic electron correlation and to ensure that all parts of the reaction path are treated equivalently, multireference second-order perturbation theory was used, since the level of accuracy for such methods is at least comparable to that of MP2 when single-reference methods are appropriate.[17] The particular version of this method used in the present work is referred to as MRMP2 (multireference second-order perturbation theory).[18] For comparison with the results of these multireference calculations, calculations have also been performed with three single-reference methods: Hartree−Fock (HF), density functional theory (DFT) with the B3LYP[19] exchange-correlation functional, and second-order Møller−Plesset perturbation theory (MP2).[20] The GAMESS (General atomic and molecular electronic structure system)[21] program was used for all of the computations.

To study surface size-effects, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called SIMOMM[22] (surface integrated molecular orbital molecular mechanics) was used. Two different SIMOMM cluster models were designed and are represented in Figure 2. For the along the dimer-row products, a $C_6H_{24}Si_{15}$ quantum region is embedded in a $C_6H_{68}Si_{80}$ cluster (Figure 2a). The calculations described in sections A through D in the Results and Discussion section were done with this cluster model. For the across the dimer-row products described in section E, a $C_6H_{32}Si_{23}$ quantum region is embedded in a $C_6H_{60}Si_{60}$ cluster (Figure 2b). In the interest of conserving computer resources, two basis sets were used for the quantum region (see Figure 2c). The 6-31G(d) and 3-21G basis sets were used for the most active part ($C_6H_{22}Si_{12}$) and the less active part ($Si_{11}H_{10}$) of the quantum region, respectively. The corresponding two basis set regions are shown in darker and lighter gray colors. MM3[23] parameters were used for the molecular mechanics optimization part of the computations. All of the computations were done without imposing symmetry unless otherwise specified.

III. Results and Discussion

Five unique reaction channels involving two surface dimers along and across the dimer-rows were identified. The resulting geometric and energetic data are presented in Chart 1 and Table 1. The separated 1,3-cyclohexadiene and bare surface serve as the reference energy point for the other stationary points on the potential energy surface.

A. 4π+2π Channel. This channel is initiated by the [4+2] cycloaddition of 1,3-cyclohexadiene and one surface dimer. Since it is symmetry-allowed, it is expected that there is a small or zero reaction barrier to the [4+2] product, **1** (see Chart 1). In the earlier study of this channel with a different SIMOMM model, a third-order saddle point was located along the symmetric path at the CASSCF(6,6)/HW(d) level of theory. An

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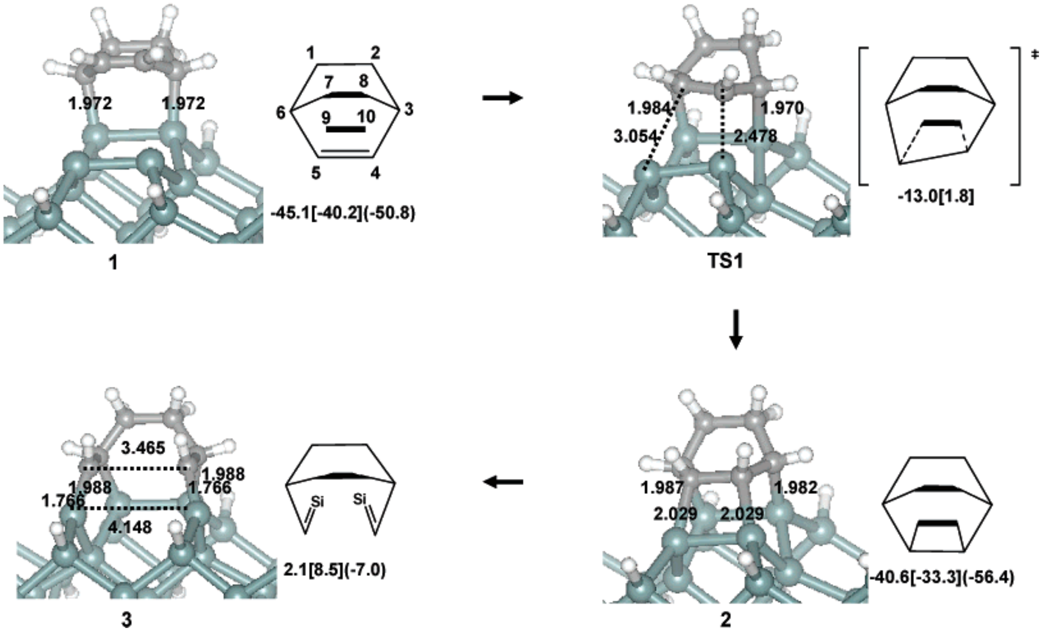
Chart 1. Geometric and Energetic Data for the 4π+2π Channel[a]



[a] Thick lines on the illustrations represent the surface Si dimers; numbers in the illustrations are the atom numbering schemes; energies relative to separated reactants in kcal/mol as obtained with SIMOMM:MRMP2/6-31G(d) are listed under the illustrations; numbers in brackets and parentheses are respectively SIMOMM:CASSCF(8,8)/6-31G(d) and SIMOMM:B3LYP/6-31G(d) relative energy values; geometries as obtained with SIMOMM:CASSCF(8,8)/6-31G(d) are presented in the structures; those obtained with SIMOMM:B3LYP/6-31G(d) are presented in parentheses; see text for detailed descriptions of each stationary point.

Table 1. MRMP2, CASSCF and DFT Relative Energies of Stable Points along the Reaction Channels in kcal/mol[a]

4π+2π	4π+2R	2π+2π	2π+2R	4π+2R[b]
1, −45.1[−40.2](−50. 8)	**TS2**, 1.7[1.6]	**TS4**, −5.5[1.8]	**TS5,** 7.3[4.5]	**TS6**, 1.6[0.03](0.09)
TS1, −13.0[1.8]	**4**−30.3[−34.3](−35.0)	**6**, −28.3[−23.1](−36. 0)	**8**, −18.7[−23.0](−18. 6)	**9**, −35.3[−41.4](−28. 8)
2, −40.6[−33.3](−56. 4)	**TS3**, −15.7[1.8]	**7**, 7.1[9.1](−21.1)		
3, 2.1[8.5](−7.0)	**5**, −26.8[−18.4](−42. 5)			

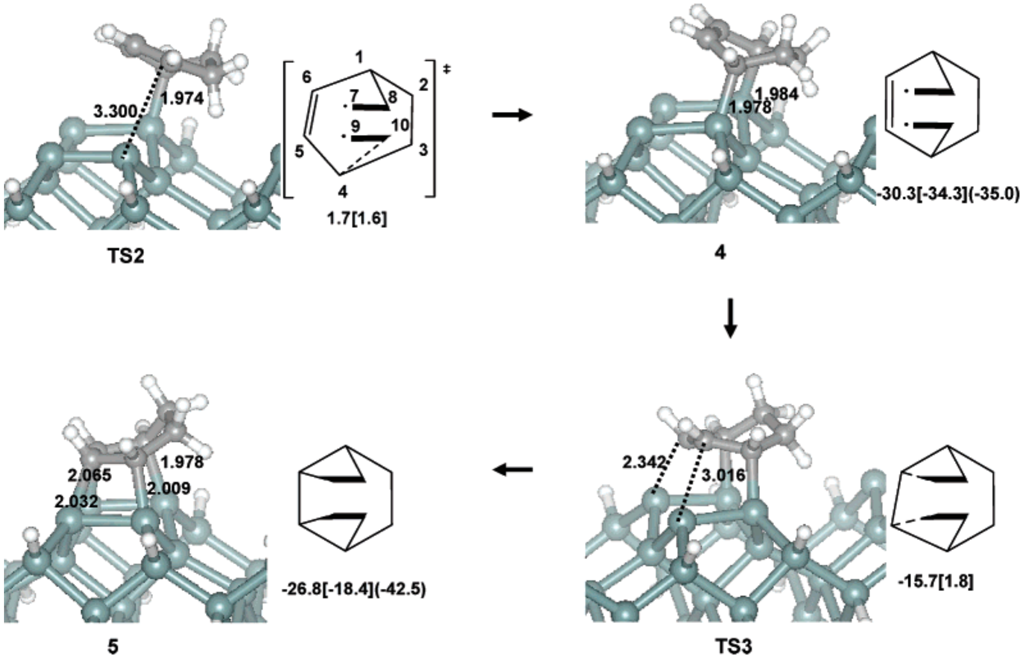
[a] The numbers are MRMP2 values; the numbers in brackets and parentheses are CASSCF and DFT values, respectively. [b] Across the dimer-row.

MRMP2 single-point energy at the CASSCF(6,6) geometry, MRMP2//CASSCF(6,6), yielded a barrier of 0.0 kcal/mol.[10] This estimate is consistent with the second-order saddle point reported previously by Konecny and Doren[8] with a 0.3 kcal/mol B3LYP/6-31G* barrier. It is expected that the barrier at a true first-order saddle point would be lower, if one exists; however, it is clearly essentially zero. MRMP2 and B3LYP predict that the [4+2] product has large thermodynamic stabilities of −45.1 and −50.8 kcal/mol, respectively. In the earlier SIMOMM study of the [4+2] reaction mechanism, **1** was the final surface product. However, the remaining C═C bond of **1** can be subjected to a further [2+2] cycloaddition with its closest neighboring SiSi dimer by forming bonds between Si9−C5 and Si10−C4 (see Chart 1). This cycloaddition isomerization path yields a tetracoordinated surface product, **2**, with MRMP2 and B3LYP stabilization energies of −40.6 and −56.4 kcal/mol, respectively, relative to the separated reactants. Although **2** has two more interfacial surface bonds than **1**, it is expected that **2** has more ring strain due to the four-membered ring. Consequently, MRMP2 predicts that **2** is less stable than **1** by 4.5 kcal/mol, while B3LYP predicts the opposite. In any case, both theories show that **2** is a thermodynamically important structure. In order for **2** to be formed at modest temperatures, the kinetic barrier to the formation of **2** needs to be reasonably small. Since a [2+2] cycloaddition, in general, is symmetry-forbidden, the symmetric (least motion) path has a large barrier. However, the new bonds C5−Si9 and C4−Si10 are formed asymmetrically via transition state **TS1** to form **2** directly from **1.** The NOON (Natural Orbital Occupation Number) values of the corresponding surface neighbor dimer are 1.36 and 0.64, indicating large diradical character. While the MRMP2 barrier height at TS1 is 32 kcal/mol relative to **1**, this transition state is still 13.0 kcal/mol below the separated reactants, so there should be sufficient energy available for **2** to be kinetically accessible from **1.** This suggests that the product distributions between **1** and **2** are likely to be determined by thermodynamics.

A reverse-[2+2] cycloaddition involving C4, C5, Si9, and Si10 from **2** can yield another stationary point, **3**, in which C4═Si10 and C5═Si9 interfacial double bonds are formed. Since C═Si bonds are considerably less stable than C═C bonds, isomer **3** is 2.1 kcal/mol (MRMP2) higher in energy than the separated reactants and nearly 47 kcal/mol higher in energy than isomer **1**. Due to this relative thermodynamic instability, **3** may not be an important stationary point along this channel, except in the high-temperature regime. Therefore, no further investigation on the TS connecting **2** and **3** was performed.

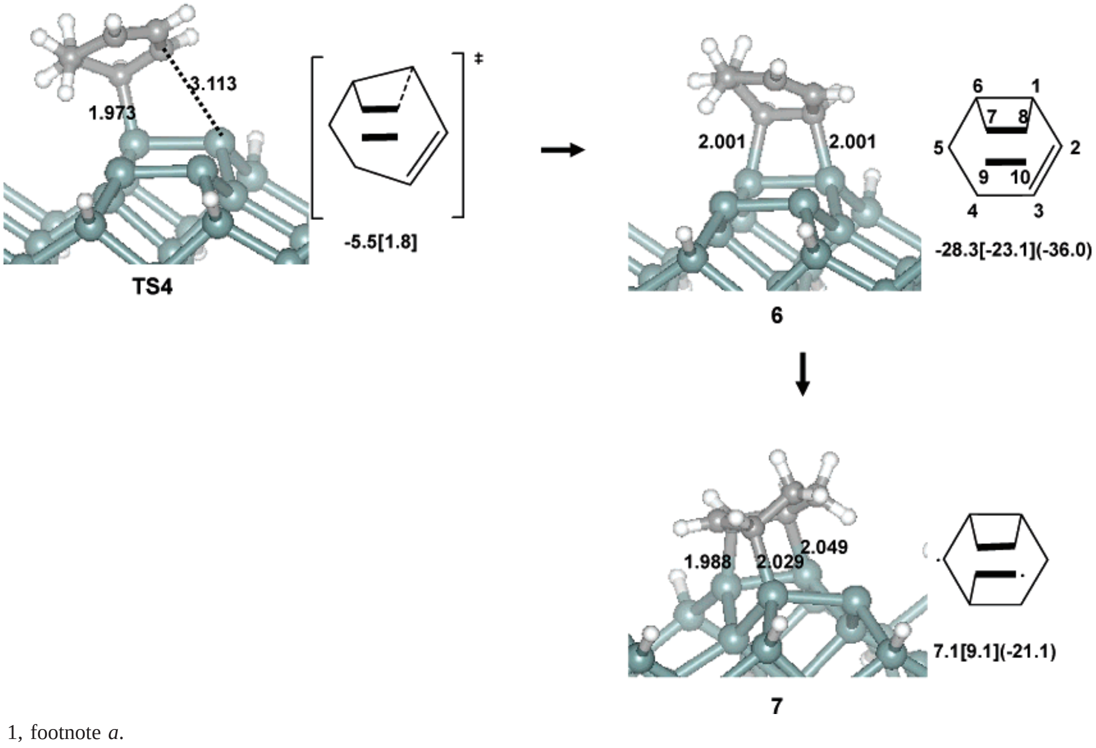
B. 4π+2R Channel. The [4+2] reaction along the Si dimer-row creates a unique surface diradical, **4** (see Chart 2). The NOONs of the corresponding diradical orbitals are 1.09 and 0.91, indicating a nearly singlet diradical. Teague and Boland[13] recently reported, on the basis of an experimental STM study, that the surface structure **1c** (see Figure 1), in which two

Chart 2. Geometric and Energetic Data for the 4π+2R Channel[a]



[a] See Chart 1, footnote *a*.

Chart 3. Geometric and Energetic Data for the 2π+2π Channel[a]

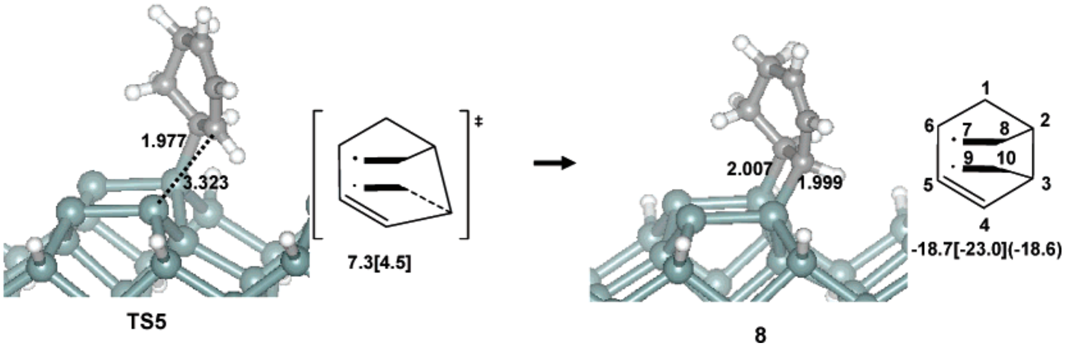


[a] See Chart 1, footnote *a*.

interfacial Si−C bonds are formed on two different Si dimers in a row, is the dominant surface species. In the present work, CASSCF as well as B3LYP geometry optimizations find the [4π+2R] product, **4**, to be a stationary point on the potential energy surface, with MRMP2 and B3LYP energies of −30.3 and −35.0 kcal/mol, respectively, relative to separated reactants. So, although **4** is less stable than **1** and **2** as a result of its diradical nature**,** it appears to be thermodynamically important.

The asymmetric transition state, **TS2**, leading to product **4** has an MRMP2 energy that is 1.7 kcal/mol above that of the separated reactants. So, even though **TS2** is nearly 47 kcal/mol above **1** and approximately isoenergetic with **3**, it is likely that the product **4** is also kinetically accessible. The NOON values of important orbitals of **TS2** are 1.01, 0.99, 1.52, and 0.48, showing highly multi-configurational character that cannot easily be described by a single reference method. As for **1**, the product **4** has a remaining C═C bond that can further undergo [2π+2R] reactions with the surface diradical dimer. This isomerization reaction leads to another tetra-coordinated product, **5**, with MRMP2 and B3LYP stabilization energies of −26.8 and −42.5

Chart 4. Geometric and Energetic Data for the 2π+2R Channel[a]



[a] See Chart 1, footnote *a*.

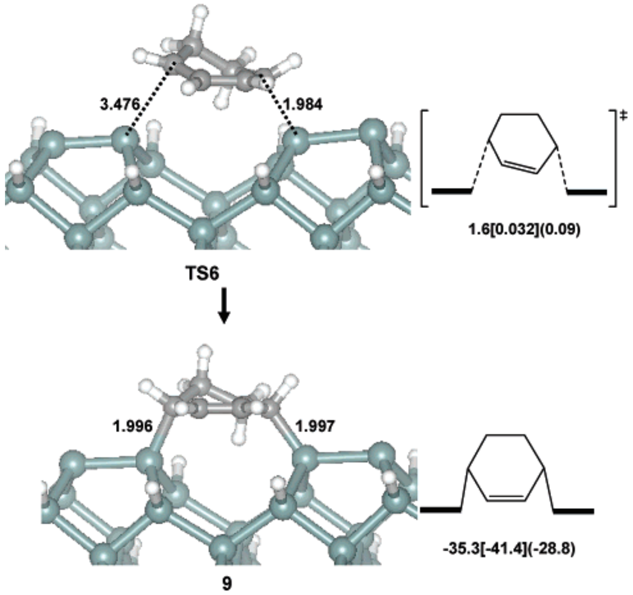
kcal/mol, respectively. So, the new species, **5**, is as stable as **4**. The stability of **5** is the result of compensating effects between the two additional interfacial Si−C bonds and the ring strain of two four-membered rings. The asymmetric transition state, **TS3**, connecting **4** and **5** has an MRMP2 net barrier of −15.7 kcal/mol, indicating that the product **5** is also kinetically accessible from **4**. In short, the two possible surface products **4** and **5** of this channel are both thermodynamically stable and kinetically accessible.

C. 2π+2π Channel. It has been shown[10] that the [2+2] product, **6**, can be formed easily on the Si(100) surface, even though it is about 20 kcal/mol less stable than the most stable [4+2] product, **1**. The current two-dimer SIMOMM model yields a similar stability for the [2+2] product **6** (see Chart 3). An asymmetric transition state, **TS4**, was located as an initial barrier (from separated reactants) to the [2+2] product with a small MRMP2 internal barrier of −5.5 kcal/mol. The NOON values of the important orbitals are 1.46, 0.54, 1.65, and 0.35, also exhibiting large multi-configurational character. Making an interfacial bond between C4 and Si9 yielded a tri-bonded diradical product, **7**. However, the MRMP2 relative energy of 7.1 kcal/mol shows that it may not be an important structure. As expected, the NOON values of 1.09 and 0.91 indicate a nearly diradical character. A TS connecting structures **6** and **7** was not located.

D. 2π+2R Channel. Although it has not been suggested, an inter-row 2π+2R path is also possible. The initial product on this path, **8**, has an MRMP2 stabilization energy of 18.7 kcal/mol (see Chart 4). Although it is not as stable as other predicted surface products, **8** may still be an important thermodynamic structure. The stability of **8** may be reduced due to the short C2−C3 bond length as compared to the long Si8−Si10 distance, resulting in some ring strain. As in the product **4**, the corresponding NOON values of **8** are 1.01 and 0.99. **TS5** leading to **8** from separated reactants has an MRMP2 relative energy of 7.3 kcal/mol, showing that this channel has a higher barrier than the other products mentioned previously. Therefore, product **8** may not be an important initial product. Nonetheless it may still be a good surface product candidate for the high-temperature environment. The NOON values of **TS5** are 1.07, 0.93, 1.48, and 0.52, indicating a highly multi-configurational character.

E. 4π+2R Channel across the Dimer-Row. To study this part of the potential energy surface, the second SIMOMM model (see Figure 2b) in which a $C_6H_{32}Si_{23}$ quantum region is embedded in a $C_6H_{60}Si_{60}$ cluster was employed. Detailed descriptions of this model can be found in the Computational Details section.

Chart 5. Geometric and Energetic Data for the 4π+2R Channel[a]



[a] See Chart 1, footnote *a*.

The initial product, **9**, of this channel is a minimum on the CASSCF and the DFT potential energy surfaces, with an overall MRMP2 stabilization energy of 35.3 kcal/mol (see Chart 5). This is lower in energy than the products **4**, **5**, **6**, and **8**. The surface product **9** was suggested by the experiments of Teague and Boland,[13] as discussed in the Introduction. An asymmetric transition state **TS6** leading to **9** from separated reactants has a MRMP2 barrier of 1.6 kcal/mol. Such a small barrier indicates that the surface product **9** may be kinetically accessible.

IV. Conclusions

The initial and the subsequent surface reaction mechanisms of 1,3-cyclohexadiene on the Si(100)-2×1 surface were explored with the help of multireference as well density functional theories. Five different initial reaction channels leading to nine different surface products were identified. Among these, surface products **2**, **3**, **5**, **7**, and **8** are new species that have not been reported before. Although **3** and **7** are only marginally stable, the other seven products are thermodynamically important and kinetically accessible, and therefore they may exist. Structure **8** may require some thermal energy to be formed. Therefore, it is hoped that subsequent experimental studies will detect at least species **2** and **5**. Many of the species have significant diradical character, as illustrated by the occupation numbers of their natural orbitals, so the use of a multireference wave function is essential.

Transition-state studies revealed that reaction barriers within the same channel are sufficiently below the energy of the separated reactants that the final product distributions within the same channel should be determined by thermodynamics. It was shown earlier[10] that the thermal isomerizations between products of the [$4\pi+2\pi$] and [$2\pi+2\pi$] channels are not expected to occur easily. If this conclusion can be extended to the other reaction channels found in this paper, it can be seen that the surface product distributions among the five *different* channels are more likely to be determined by kinetics. Possible surface thermal isomerizations among the alternative reaction channels are currently being explored to better resolve this issue.

The current study shows that the interplay between the thermodynamics, kinetics, and mechanisms of the diene on the Si(100) surface are more complex then previously known. To better understand these surface reactions, one really must consider the several reaction-determining factors collectively.

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