

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230597830>

# Cycloaddition Reactions of 1,3-Cyclohexadiene on the Silicon(001) Surface

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · DECEMBER 1999

Impact Factor: 12.11 · DOI: 10.1021/ja9914285

---

CITATIONS

112

---

READS

23

2 AUTHORS, INCLUDING:



Cheol Ho Choi

Kyungpook National University

111 PUBLICATIONS 2,104 CITATIONS

SEE PROFILE

# Cycloaddition Reactions of 1,3-Cyclohexadiene on the Silicon(001) Surface

Cheol Ho Choi and Mark S. Gordon\*

Contribution from Ames Lab, 201 Spedding Hall, Iowa State University, Ames, Iowa 50011

Received May 3, 1999

**Abstract:** [2+2] and [4+2] cycloaddition reactions of 1,3-cyclohexadiene on the Si(001) surface were studied. It is shown that not only the [4+2] cycloaddition reaction but also the [2+2] cycloadditions can occur on the Si(001) surface. Surface isomerization reactions connecting [4+2] and [2+2] are very unlikely due to a high energy barrier, implying that the surface reactions are kinetically controlled. Therefore the final surface reaction products are determined during the initial stage of the reactions in contrast with earlier assumptions that the “product distribution is thermodynamically determined”. Our interpretations are consistent with the new experimental results by the Hamers group. According to our CASSCF(6,6) calculations, the nonsymmetric  $\pi$ -complex transition states along the [2+2] cycloaddition mechanism, which has been suggested by many theoretical studies, seem to be an artifact. Nevertheless, the very soft Si dimer buckling motion of the Si(001) surface certainly facilitates the [2+2] reaction.

## Introduction

Surfaces of solid state materials are chemically active due to the existence of under-coordinated atoms. An active surface is likely to undergo relaxation and reconstruction to be stabilized. However, such processes are hindered by the latent structural resistance of subsurface layers. Consequently, the chemistry on the surface is determined not only by the atoms of the surface but by their subsurface layers as well.

Over the past three decades, chemical reactions on silicon surfaces have been intensely studied because of their technological importance.<sup>1</sup> Of particular interest for device fabrication is the Si(001) surface, formed when bulk Si is cleaved perpendicular to the(001) lattice direction. On the native Si-(001) surface, each Si atom has two dangling bonds, so it is energetically favorable for adjacent Si atoms to form dimers. These dimer bonds have been described by a  $\sigma$  bond and a weak  $\pi$  bond.<sup>2</sup> Redondo and Goddard<sup>3</sup> have shown these are more correctly viewed as a singlet diradical, an important distinction, since the latter require a multireference wave function for an adequate description. More recently, Paulus<sup>4,5</sup> has examined silicon clusters of varying size and confirmed the notion that multireference wave functions are necessary for a proper description of surface dimers. Both symmetric and buckled dimers are experimentally observed and theoretically predicted on the Si(001) surface.<sup>6</sup> However, recent extensive theoretical studies<sup>4</sup> showed that the symmetric dimer is the minimum. A lesson from previous experimental and theoretical studies may be the forces that distinguish between the buckled and unbuckled structures are very subtle. Consequently, whether they are

buckled or not, their contributions to the potential energy surface seem to be relatively small, whereas their impact on reactivity may be quite large.

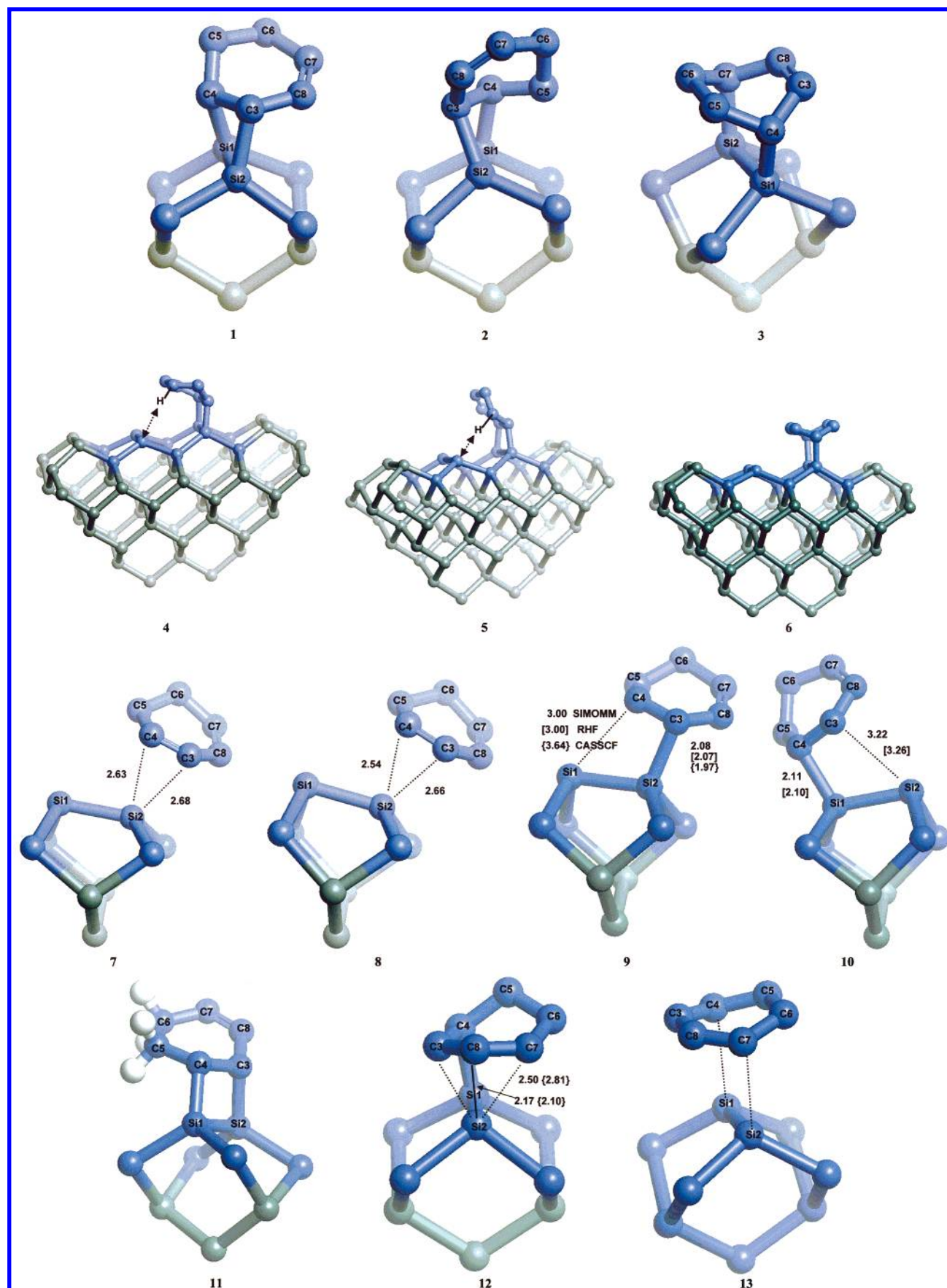
Indeed, such rather nonrigid chemical bonds are manifested by their high reactivity. The direct addition of a single C–C  $\pi$  bond to the Si dimer on the Si(001) surface seems to constitute a  $2s+2s$  cycloaddition, which is orbital symmetry forbidden.<sup>7</sup> However, it has been known that unsaturated hydrocarbons<sup>8</sup> such as acetylene, ethylene, and propylene can readily react with the Si(001) surface. In contrast, analogous [2+2] reactions of disilenes have been found to be extremely slow.<sup>9</sup> In the case of acetylene on the Si(001) surface, Liu and Hoffmann<sup>6c</sup> have suggested a nonconcerted reaction composed of a  $\pi$ -complex precursor and a biradical intermediate.

On the other hand, the well-known [4+2] or “Diels–Alder” cycloaddition can also occur at the Si(001) surface. The [4+2] cycloaddition produces a six-membered ring that is less strained than the four-membered ring produced by the [2+2] cycloaddition. Therefore, the [4+2] products are expected to be thermodynamically more stable than the [2+2] products. In the

(1) Waltenberg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, 95, 1589.  
 (2) (a) Appelbaum, J. A.; Baraff, G. A.; Hamann, D. R. *Phys. Rev. B* **1976**, 14, 588. (b) Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B* **1986**, 34, 5343. (c) Radeke, M. R.; Carter, E. A. *Annu. Rev. Phys. Chem.* **1997**, 48, 243.  
 (3) Redondo, A.; Goddard, W. A., III *J. Vac. Sci. Technol.* **1982**, 21 (2), 344.  
 (4) Paulus, B. *Surf. Sci.* **1998**, 408, 195.  
 (5) Shoemaker, J. R.; Burgraff, L. W.; Gordon, M. S. *J. Chem. Phys.* In press.

(6) (a) Chadi, D. J. *Phys. Rev. Lett.* **1979**, 43, 43. (b) Tromp, R. M.; Hamers, R. J.; Demuth, J. E. *Science* **1986**, 234, 304. (c) Roberts, N.; Needs, R. J. *Surf. Sci.* **1990**, 236, 112. (d) Men, F. K. *Phys. Rev. B* **1994**, 50, 15469. (e) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, 117, 4082. (f) Uchikawa, M.; Ishida, M.; Miyake, K.; Hata, K.; Yoshizaki, R.; Shigekawa, H. *Surf. Sci.* **1996**, 369, 424. (g) Doren, D. J.; Robinson, B. A.; Konecny, R. In *Control of Semiconductor Surfaces and Interfaces*; Prokes, S. M., Glembocki, O. J., Brierley, S. K., Woodall, J. M., Eds.; Materials Research Society: Pittsburgh, PA, 1997.  
 (7) Woodward, R. B.; Hoffmann, R. *The conservation of orbital symmetry*; VCH: Weinheim, 1970.  
 (8) (a) Yates, J. T. *J. Phys.: Condens. Matter* **1991**, 3, S43. (b) Bozack, M. J.; Taylor, P. A.; Choyke, W. J.; Yates, J. T. *J. Surf. Sci.* **1986**, 177, L933. (c) Taylor, P. A.; Wallace, R. M.; Cheng, C. C.; Weinberg, W. H.; Dresser, M. J.; Choyke, W. J.; Yates, J. T. *J. Am. Chem. Soc.* **1992**, 114, 6754. (d) Clemen, L.; Wallace, R. M.; Taylor, P. A.; Dresser, M. J.; Choyke, W. J.; Weinberg, W. H.; Yates, J. T. *Surf. Sci.* **1992**, 268, 205. (e) Cheng, C. C.; Wallace, R. M.; Taylor, P. A.; Choyke, W. J.; Yates, J. T. *J. Appl. Phys.* **1990**, 67, 3693. (f) Cheng, C. C.; Choyke, W. J.; Yates, J. T. *J. Surf. Sci.* **1990**, 231, 289.  
 (9) (a) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 1201. (b) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, 106, 7677.

Chart 1



case of the adsorption of 1,3-cyclohexadiene on the Si(001) surface, Konecny and Doren<sup>10</sup> predicted that the [4+2] product is more stable than the [2+2] product by 15.2 kcal/mol. They

also showed that the predicted vibrational spectra of the Diels–Alder products of the 1,3-butadiene and 2,3-dimethyl-1,3-butadiene are consistent with the observed spectra<sup>11</sup> and

inconsistent with significant formation of [2+2] addition product. The corresponding experimental results<sup>11</sup> for the adsorption of 2,3-dimethyl-1,3-butadiene and 1,3-butadiene on the Si(001)-(2 × 1) surface showed exclusive evidence for only the [4+2] product. These two theoretical and experimental studies seem to establish the notion of thermodynamically controlled surface reactions of dienes on the Si(001) surface. In drawing their main conclusion, Konecny and Doren assumed that "the product distribution is thermodynamically determined". In other words, the isomerization reaction between [4+2] and [2+2] products has little or no reaction barrier. Therefore, according to their argument, even if the [2+2] reaction product is formed initially, it will be soon converted to the [4+2] product.

However, more recent experiments by the Hamers group<sup>12</sup> indicate the existence of competition between [4+2] and [2+2] cycloaddition reactions of 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene on the Si(001) surface. They concluded that "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".

The primary issue is whether the final products are determined by the initial stage of reactions, or if the initial products are subject to subsequent surface reactions. More importantly, one must determine whether the [4+2] product is exclusively formed, since this ultimately bears on the chemical selectivity of the Si(001)-(2 × 1) surface toward conjugated diene systems.

To resolve the current apparent inconsistencies involving experiment and theory and to better understand the cycloaddition reactions of 1,3-cyclohexadiene on the Si(001) surface, we have performed full potential energy searches along the possible reaction paths. Recently, a new method, SIMOMM (Surface Integrated Molecular Orbital/Molecular Mechanics), has been proposed<sup>13</sup> for the study of surfaces. As a test, a comparison between SIMOMM and full quantum mechanical results has also been made, to show that SIMOMM is a viable method that can significantly reduce computational cost while maintaining the quality of the results.

## Computational Details

Two basis sets were used. The smaller basis set consists of the Hay–Wadt<sup>14</sup> effective core potential for the core electrons and a double- $\zeta$  plus polarization (3s3p1d/2s2p1d) basis for the valence electrons of Si atom. For the C and H atoms, the 3-21G standard basis set was used. This basis set is referred to as HW(d). The all electron basis set, DZV-(d), consists of the Dunning/Hay<sup>15</sup> double- $\zeta$  valence basis set augmented with a set of polarization functions. The 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, the intrinsic reaction coordinate (IRC), Gonzalez-Schlegel second-order method<sup>16</sup> was used with a step size of 0.3 amu<sup>1/2</sup> bohr. The restricted Hartree–Fock (RHF) level of

theory was used for the ground-state structures, the transition states, and potential energy surface, followed by single-point computations with Møller–Plesset second-order perturbation theory (MP2).

Konecny and Doren<sup>10</sup> studied the products of this cycloaddition reaction using density functional theory (DFT). This seems to be appropriate for the study of the final products, since the products are largely single configurational. However, various points on the reaction paths, particularly transition states and intermediates, are inherently multiconfigurational. Therefore, methods based on the multiconfiguration wave function with the second-order energy corrections are essential for consistent analyses of these paths. Therefore, a six-orbitals and six-electrons active space wave function, CASSCF(6,6) (complete active space SCF),<sup>17,18b</sup> was used to reoptimize structures of several important points along the reaction paths. The selected orbitals for the active space are discussed below. To recover the dynamical electron correlation, 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.<sup>18</sup> The particular version of this method used in the present work, referred to as MCQDPT2 (multi-configurational quasi-degenerate second-order perturbation theory),<sup>19</sup> was used at the CASSCF(6,6) optimized geometries. The GAMESS (general atomic and molecular electronic structure system)<sup>20</sup> program was used for all of the computations.

The differences between various QM/MM approaches arise in how the QM and MM portions of the model are linked. In IMOMM (Integrated Molecular Orbital/Molecular Mechanics),<sup>21</sup> the lengths of the connecting bonds remain fixed at user selected values. However, this linking scheme causes some problems when used for surface models. For surface models, the high degree of connectivity in a lattice means there will be a large number of links between the QM and MM regions, which results in the imposition of a large number of user-defined constraints. To correct this, SIMOMM removes the fixed geometric parameters during geometry optimization. MM3<sup>22</sup> parameters were used for the molecular mechanics optimization part of the computations.

Two different SIMOMM models were designed: one composed of a C<sub>6</sub>Si<sub>6</sub>H<sub>20</sub> quantum region embedded in a C<sub>6</sub>Si<sub>9</sub>H<sub>20</sub> cluster, and one composed of a C<sub>6</sub>Si<sub>10</sub>H<sub>24</sub> quantum region embedded in a C<sub>6</sub>Si<sub>63</sub>H<sub>57</sub> cluster. These are referred to as the smaller and larger SIMOMM models, respectively. All of the computations were done without imposing symmetry unless otherwise specified.

The GVB-PP(1)<sup>23</sup> (generalized valence bond with one correlated pair of orbitals responsible for the bonding and antibonding of the diradical) level of theory, the simplest correct model for a singlet diradical, was used when the systems have a bare Si dimer.

## Results and Discussions

**A. Surface Reaction Products.** Two different types (1 and 2 in Chart 1) of [2+2] product resulting from adsorption of

(10) (a) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098. (b) Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169.

(11) (a) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, *119*, 11100. (b) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Chem. Phys.* **1998**, *108*, 4599.

(12) Hovis, J. S.; Liu, H.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 6873.

(13) Shoemaker, J. R.; Burgraff, L. W.; Gordon, M. S. *J. Phys. Chem. A* **1999**, *103* (17), 3245.

(14) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(15) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977.

(16) (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853.

(17) (a) Sunberg, K. R.; Ruedenberg, K. In *Quantum Science*; Calais, J. L.; Goscinski, O.; Linderberg, J., Ohm, Y., Eds.; Plenum: New York, 1976. (b) Cheung, L. M.; Sunberg, K. R.; Ruedenberg, K. *Int. J. Quantum Chem.* **1979**, *16*, 1103. (c) Ruedenberg, K.; Schmidt, M.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41. (d) Roos, B. O.; Taylor, P.; Siegbahn, P. E. *Chem. Phys.* **1980**, *48*, 157.

(18) (a) Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645. (b) Schmidt, M. S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233. (c) Glaesemann, K. R.; Gordon, M. S.; Nakano, H. *PCCP* **1999**, *1*, 967.

(19) (a) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983. (b) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372.

(20) (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347. (b) Experimental version of GAMESS was used for the SIMOMM.

(21) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170.

(22) (a) Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. (b) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. (c) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.

(23) Bobrowicz, F. W.; Goddard, W. A. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976; Vol. 3, Chapter 4.



**Table 1.** Relative Energies (kcal/mol) of 1,3-Hexadiene Adsorption on the Silicon (001)-(2×1) Surface

			3/6, <sup>a</sup> [4+2]	1/4, <sup>a</sup> [2+2]	2/5, <sup>a</sup> [2+2]
SIMOMM (C <sub>6</sub> Si <sub>6</sub> H <sub>20</sub> /C <sub>6</sub> Si <sub>9</sub> H <sub>20</sub> )	RHF/HW(d)	MO+MM	0	21.7	21.8
	MP2//RHF/HW(d)	MP2+MM	0	21.5	22.3
	RHF/DZV(d)	MO+MM	0	18.6	18.3
	MP2//RHF/DZV(d)	MP2+MM	0	20.5	21.2
Full QM (C <sub>6</sub> Si <sub>9</sub> H <sub>20</sub> )	RHF/HW(d)		0	20.9	21.1
	MP2//RHF/HW(d)		0	20.3	21.3
	RHF/DZV(d)		0	17.4	17.2
	MP2//RHF/DZV(d)		0	18.7	19.5
SIMOMM (C <sub>6</sub> Si <sub>10</sub> H <sub>24</sub> /C <sub>6</sub> Si <sub>63</sub> H <sub>57</sub> )	GVB-PP(1)/HW(d)	MO+MM	0	20.8	21.1
	MCQDPT//GVB-PP(1)/HW(d)	MP2+MM	0	20.6	22.4

<sup>a</sup> See Chart 1.

1,3-cyclohexadiene on the Si(001)-(2×1) surface are found, depending on the conformation of the two sp<sup>3</sup> carbons of 1,3-cyclohexadiene. The atoms colored in purple were treated quantum mechanically in the SIMOMM scheme and the others by molecular mechanics. Full quantum mechanical results simply include all of the atoms in the ab initio computations. Table 1 summarizes the relative stabilities of **1** and **2** as compared to [4+2] product, **3**. The relative energies of **1** and **2** with respect to **3** calculated with the SIMOMM:RHF/HW(d) (C<sub>6</sub>Si<sub>6</sub>H<sub>20</sub>/C<sub>6</sub>Si<sub>9</sub>H<sub>20</sub>) scheme are 21.7 and 21.8 kcal/mol, respectively. (Note that these SIMOMM relative energies are based on the total energies composed of QM and MM energies.<sup>13</sup>) The MP2 relative energies are essentially the same, so there is little effect of correlation on the overall reaction energy. The larger basis set, DZV(d), yields similar results. Most importantly, the SIMOMM scheme reproduces the results of full quantum mechanical methods quantitatively. Our results are consistent with an earlier theoretical study<sup>10</sup> and predict that the [4+2] product is thermodynamically more stable than the [2+2] products.

As indicated by two-headed arrows in **4** and **5**, because of their close distance, some interactions seem to be possible between the indicated hydrogen and one of the dimerized first neighbor silicon atoms of the surface. Larger SIMOMM clusters (C<sub>6</sub>Si<sub>10</sub>H<sub>24</sub> QM region embedded in the C<sub>6</sub>Si<sub>63</sub>H<sub>57</sub> cluster, **4**, **5**, and **6**) were designed to study this potential effect on the relative stabilities of reactants and products. Since there is a bare Si dimer in the larger SIMOMM clusters, the GVB-PP(1)/HW(d) followed by MCQDPT2 method was used to correctly model the electronic structures and the results are presented in Table 1. However, the trend as computed with the larger SIMOMM clusters is nearly the same as other smaller cluster results showing that the first neighbor Si dimer does not interact much with the adsorbate.

Some selected geometric parameters optimized with SIMOMM and full QM methods are collected in Table 2. Comparison of the SIMOMM results with the corresponding full QM results illustrates differences in bond lengths on the order of 0.001 Å. This again shows that SIMOMM reproduces full QM results extremely well regardless of the basis set used. The effect of the first neighbor Si dimer on the geometric parameters is small as shown in the results for the larger SIMOMM cluster models. Since the DZV(d) basis set and larger SIMOMM cluster have only a small effect on the quantitative results, the HW(d) basis set and smaller SIMOMM cluster were used for the rest of the calculations discussed below.

**B. [2+2] Cycloaddition Mechanism.** Although the [4+2] product is thermodynamically more stable by about 20 kcal/mol as compared to the [2+2] products, it is still possible that kinetic factors might change the relative abundance of the final products. The [2<sub>s</sub>+2<sub>s</sub>] reaction is apparently symmetry-forbidden

**Table 2.** Selected Geometric Parameters(Å)

		Si <sub>1</sub> –C <sub>4</sub> <sup>a</sup>	Si <sub>1</sub> –Si <sub>2</sub> <sup>a</sup>	Si <sub>2</sub> –C <sub>3</sub> / Si <sub>2</sub> –C <sub>7</sub> <sup>a,b</sup>	C <sub>3</sub> –C <sub>4</sub> <sup>a</sup>
<b>1</b>	SIMOMM:RHF/HW(d)	1.934	2.316	1.940	1.596
	RHF/HW(d)	1.936	2.312	1.944	1.595
	SIMOMM:RHF/DZV(d)	1.947	2.353	1.952	1.573
	RHF/DZV(d)	1.949	2.352	1.954	1.572
<b>2</b>	SIMOMM:RHF/HW(d)	1.933	2.320	1.935	1.599
	RHF/HW(d)	1.935	2.314	1.939	1.599
	SIMOMM:RHF/DZV(d)	1.944	2.357	1.949	1.574
	RHF/DZV(d)	1.945	2.357	1.951	1.574
<b>3</b>	SIMOMM:RHF/HW(d)	1.918	2.336	1.918	
	RHF/HW(d)	1.918	2.338	1.918	
	SIMOMM:RHF/DZV(d)	1.933	2.374	1.933	
	RHF/DZV(d)	1.934	2.379	1.934	
<b>4</b>	SIMOMM:GVB-PP(1)/HW(d)	1.939	2.313	1.941	1.598
	SIMOMM:GVB-PP(1)/HW(d)	1.936	2.312	1.934	1.611
<b>6</b>	SIMOMM:GVB-PP(1)/HW(d)	1.923	2.331	1.923	

<sup>a</sup> See Chart 1. <sup>b</sup> Bond length are Si<sub>2</sub>–C<sub>3</sub> for **1**, **2**, **4**, and **5** and Si<sub>2</sub>–C<sub>7</sub> for **3** and **6**.

according to the Woodward–Hoffmann rules; however, the reaction might proceed via a nonsymmetric pathway. At the RHF/HW(d) level of theory, we have located three transition states (**7**, **9**, and **10** in Chart 1) and one intermediate structure (**8**) along the nonsymmetric reaction path leading to the [2+2] product (see Table 3). **7** may be thought of as a  $\pi$ -complex transition state. The asymmetric structure of the surface Si dimer in **7**, where one of the Si atoms of the Si dimer is buckled-up and the other down, will lead to a gradient in the electron density, which Liu and Hoffmann<sup>6d</sup> interpreted in terms of a nucleophilic “buckled-up” Si and electrophilic “buckled-down” Si. Hovis et al.<sup>12</sup> also reported this  $\pi$ -complex. The activation barrier was estimated to be 0.3 and 0.5 kcal/mol<sup>24</sup> using RHF/HW(d) and MP2//RHF/HW(d), respectively (see Table 3). These results show that the reaction path is so flat that the 1,3-cyclohexadiene virtually feels no barrier along this approach to the surface (see Figure 1). The Si–C distances in the  $\pi$  complex **8** are 2.54 and 2.66 Å, slightly reduced from their corresponding distances in **7**. Due to the very flat potential, our SIMOMM model could not find the  $\pi$ -complex **8** nor its transition state **7**.

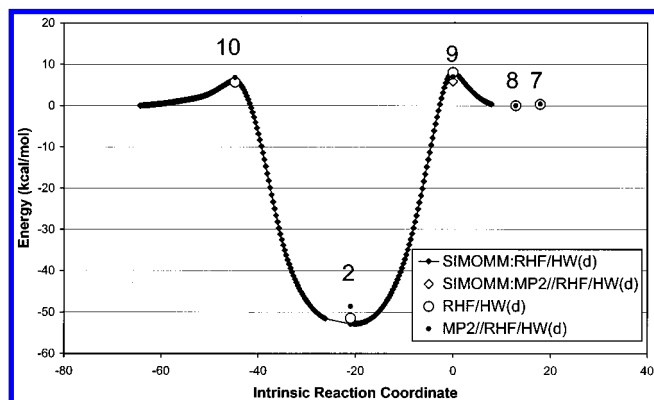
To assess the validity of the predicted  $\pi$  complex, a CASSCF-(6,6) wave function was used to re-optimize the structure of **8**. The active space used for this calculation consisted of the four  $\pi$  and  $\pi^*$  orbitals of the diene and the analogous  $\pi$  orbitals of the silicon dimer. The result of this CASSCF re-optimization of the geometry is that the  $\pi$  complex disappears. So, the proposed  $\pi$ -complex intermediate is an artifact of using a single-configurational wave function. Nonetheless, as Sheomaker et al. have shown, the very flat potential energy surface along the

(24) The activation barrier was estimated with respect to the lowest energy point of the left-hand side IRC (Intrinsic reaction coordinate) of **10** (see Figure 1).

**Table 3.** Relative Stability (kcal/mol) of the Structures along the [2+2] Cycloaddition Mechanism

	reactant	7	8	9	2	10
SIMOMM:RHF/HW(d)	0 <sup>a</sup>			8.1	-52.8	6.1
SIMOMM:MP2//RHF/HW(d)	0 <sup>a</sup>			5.9	-52.0	6.1
RHF/HW(d)	0 <sup>a</sup>	0.3	0.0	8.0	-51.5	5.6
MP2//RHF/HW(d)	0 <sup>a</sup>	0.5	0.0	7.0	-48.6	6.8
CASSCF(6,6)/HW(d)	0 <sup>b</sup>			7.7 (4.6) <sup>c</sup>	-33.1 (-34.3) <sup>c</sup>	
MCQDPT2//CASSCF(6,6)/HW(d)	0 <sup>b</sup>			8.4 (5.3) <sup>c</sup>	-37.5 (-38.7) <sup>c</sup>	

<sup>a</sup> The reference energies were estimated with respect to the lowest energy point of the left-hand side IRC of **10** (see Figure 1). <sup>b</sup> Since MCQDPT is not size-consistent, the reference energies were estimated by performing a cluster calculation where the reactants are separated by 20 Å. <sup>c</sup> Numbers in parentheses are zero-point energy corrected values.

**Figure 1.** The SIMOMM:RHF/HW(d) potential energy surface along the intrinsic reaction coordinate of [2+2] cycloaddition reaction.

buckling motion (about 200 cm<sup>-1</sup>)<sup>5</sup> clearly facilitates the initial attack of adsorbate to the Si dimer.

A transition state, **9** connecting reactants and [2+2] product, was located with a barrier of about 8 kcal/mol at both the RHF and SIMOMM:RHF levels of theory (see Table 3). This barrier is reduced to 5.9–7.0 kcal/mol with MP2 corrections. The SIMOMM optimized Si–C distances in **9** are 3.00 and 2.08 Å. The corresponding full QM values are 3.00 and 2.07 Å, showing that SIMOMM reproduces not only the relative energies, but also the transition state geometries predicted by the full QM results. A similar transition state was located with CASSCF(6,6)/HW(d) followed by a single-point energy correction at the MCQDPT2 level. The CASSCF orbitals included in the active space were the remaining two  $\pi$  orbitals ( $\pi$  and  $\pi^*$ ) of the diene and the bonding and antibonding C<sub>3</sub>–Si<sub>2</sub>  $\sigma$ -orbitals and the weak C<sub>4</sub>–Si<sub>1</sub> bond and antibond orbitals. These orbitals are presented in Figure 2 along with the natural orbital occupation numbers of each orbital. The bond length of the weak C<sub>4</sub>–Si<sub>1</sub> bond is calculated to be 3.64 Å, considerably longer than the RHF values. Since the occupation numbers of these C<sub>4</sub>–Si<sub>1</sub> bonding and antibonding orbitals are 1.07 and 0.93, as shown in Figure 2, the system is a diradical. Therefore, a single configuration is not adequate, yielding a bond that is much too short. The estimated barriers at **9** relative to reactants are 7.7 (4.6, zero-point energy corrected value) and 8.4 (5.3) kcal/mol at the CASSCF(6,6) and MCQDPT2//CASSCF(6,6) levels of theory, respectively. All calculations consistently predict the barrier to be a relatively small 4–8 kcal/mol.

Since cyclohexadiene is not symmetric with respect to the two Si atoms of the dimer due to the location of the double bonds of cyclohexadiene, another transition state **10** is possible, which is different from **9**. The existence of the transition state **10** illustrates the existence of an alternative reaction path (left-hand side of Figure 1). Unlike the right-hand side path, the  $\pi$ -complex TS and intermediate were not found even with the RHF method. This may be due to steric hindrance between the hydrogens of sp<sup>3</sup> carbons of cyclohexadiene and the surface.

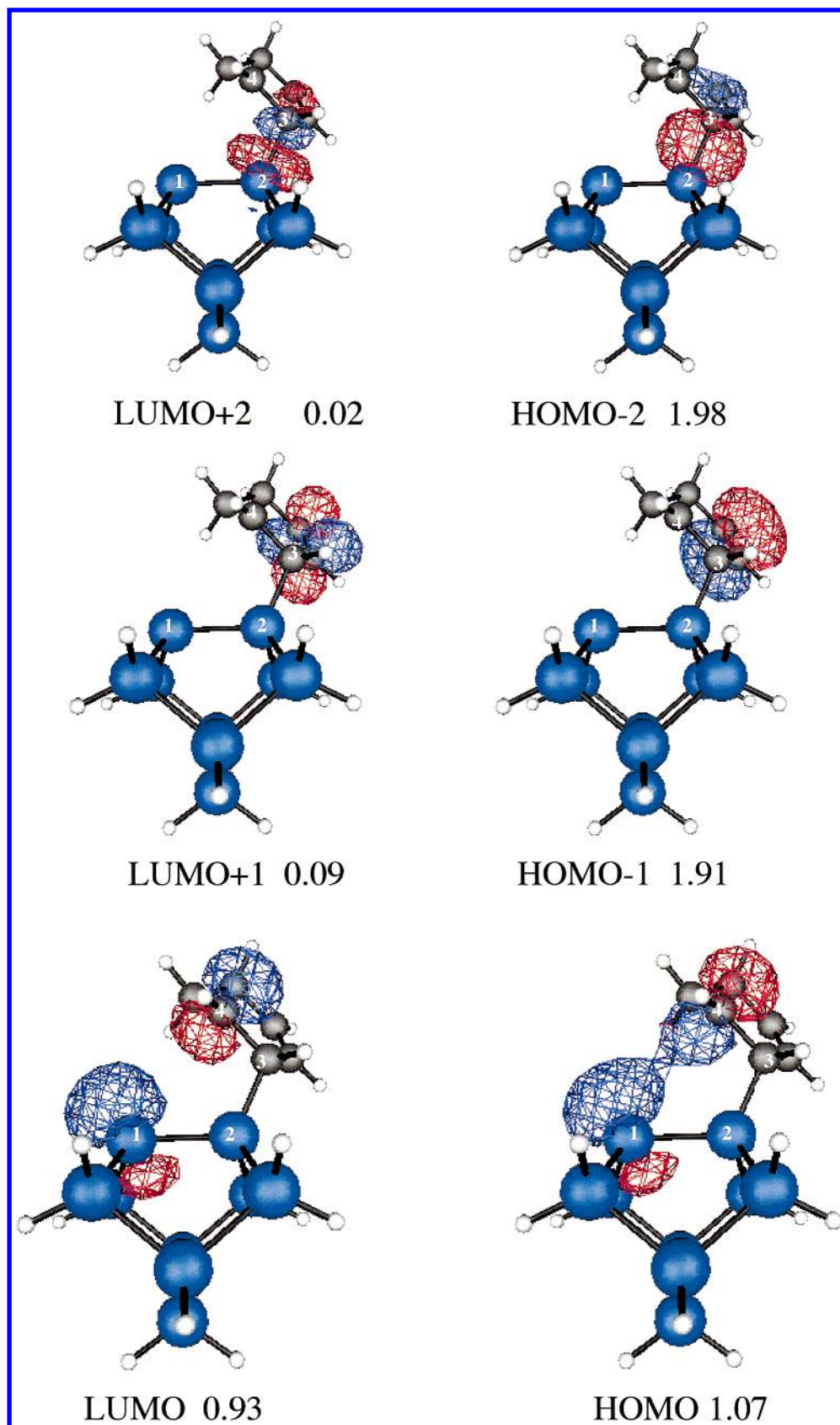
The barrier for **10** relative to reactants is calculated to be 5.6–6.8 kcal/mol with RHF/HW(d) and MP2//RHF/HW(d), respectively, nearly the same as those of TS **9**.

Potential energy surface scans along the [2+2] cycloaddition reaction surface clearly reveal that there are low-energy paths along nonsymmetric pathways indicating the possibility of having [2+2] cycloaddition products of 1,3-cyclohexadiene on the Si(001) surface. Whether there is a  $\pi$ -complex TS, **7**, or not, the buckling of the Si dimer seems to reduce the initial reaction barrier of the nonsymmetric [2+2] cycloaddition reaction in a quite nonconcerted fashion. It is encouraging to see that SIMOMM well reproduces most of the important full QM results even for the transition states. Therefore, only the SIMOMM method was used for the study reported in the next section.

### C. Isomerization Reaction of [4+2] and [2+2] Products.

Although we have demonstrated the existence of low-energy paths to [2+2] products, if there is a small reaction barrier for the isomerization connecting the [4+2] and [2+2] products as assumed by Konecny and Doren,<sup>10</sup> the final product will be determined by thermodynamics. If this is the case, one would expect to observe only [4+2] products on the surface. We have located two transition states with SIMOMM:RHF as well as SIMOMM:CASSCF(6,6), **11** and **12**, along the isomerization reaction path connecting **2** and **3**. The energetics are given in Table 4. TS **11**, which has an eclipsed conformation between the two sp<sup>3</sup> carbons of 1,3-cyclohexadiene, connects the two [2+2] products, **1** and **2** (see Figure 3). The SIMOMM reaction barrier is ~9.0 kcal/mol for both RHF and MCSCF wave functions. The MP2 energy correction does not change the height of the barrier. This barrier appears to be small enough to permit isomerization between the two [2+2] products at moderate temperatures. TS **12**, in which one of the Si–C bonds of the [2+2] product is being broken and that of the [4+2] product is being formed, connects the [2+2] product, **1**, and [4+2] product, **3**. The barriers for this reaction are 56.5 and 53.7 kcal/mol using SIMOMM:RHF and SIMOMM:CASSCF(6,6), respectively. The single-point MP2 and MCQDPT2 corrections reduce these barriers to 43.9 and 42.2 kcal/mol, respectively. However, the barrier is still significant enough to prevent the surface isomerization reaction between **1** and **3**. Hamers and co-workers<sup>12</sup> reported that surface annealing does not lead to isomerization to the [4+2] product but instead leads to desorption. Our theoretical results are consistent with their observations.

**D. [4+2] Cycloaddition Mechanism.** Since the ordinary [4+2] cycloaddition reaction is symmetry-allowed, it is expected that there is a small or zero reaction barrier to [4+2] product, **3**, even along a symmetric reaction pathway. A third-order saddle point, **13**, was located along the symmetric path at the RHF/HW(d) and CASSCF(6,6)/HW(d) levels of theory with barriers of 8.9 and 11.2 kcal/mol, respectively. The single-point energy corrections of the barriers at MP2 and MCQDPT2 give



**Figure 2.** The orbitals included in CASSCF(6,6)/HW(d) calculations of **9** along with their natural orbital occupation numbers.

barriers of 4.1 and 0.0 kcal/mol.<sup>25</sup> These estimates are consistent with the second-order saddle point reported earlier<sup>9</sup> with a 0.3

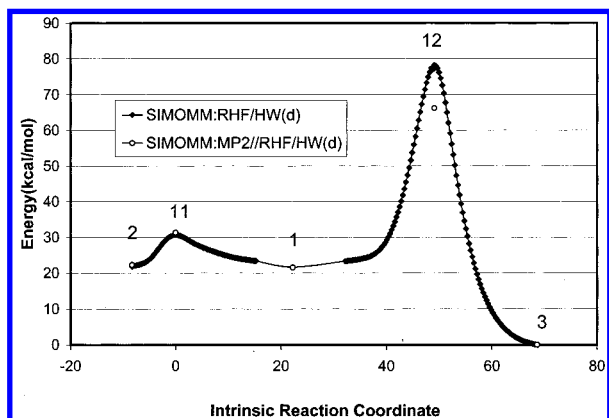
(25) It is noted that the reference energy points are different between RHF and CASSCF geometries. Therefore, MCQDPT2 energy should be more reliable.

kcal/mol barrier as calculated with B3LYP<sup>26</sup>/6-31G\*. Although a third-order saddle point does not provide the true lowest energy reaction path, it is apparent that the [4+2] addition occurs with little or no barrier. For this reason, no asymmetric saddle point was found.



**Table 4.** Relative Stability (kcal/mol) of the Structures along the Isomerization between [2+2] and [4+2] Products

	3	12	1	11	2
SIMOMM:RHF/HW(d)	0	78.2	21.7	30.6	21.8
SIMOMM:MP2//RHF/HW(d)	0	66.2	21.5	31.3	22.3
SIMOMM:CASSCF(6,6)/HW(d)	0	68.8	15.1	23.9	
SIMOMM:MCQDPT2//CASSCF(6,6)/HW(d)	0	60.6	18.4	27.6	

**Figure 3.** The SIMOMM:RHF/HW(d) potential energy surface along the intrinsic reaction coordinate of surface isomerization reaction between the [2+2] and [4+2] products.

## Conclusions

The cycloaddition reactions of 1,3-cyclohexadiene on the Si(001)-(2×1) surface were studied with the help of quantum chemical methods and our newly developed SIMOMM method. By comparing the results of the smaller and larger SIMOMM models, it is concluded that the first neighbor Si dimer has little or no effect on the adsorbate. Unlike the ordinary [2+2] cycloaddition, the existence of a surface-enhanced low-energy pathway to the [2+2] products was demonstrated, implying that the latent structural resistance of subsurface layers to the surface relaxation seems to make the surface reactive.

Three transition states and one intermediate were located along the [2+2] reaction mechanism, which constitutes a nonsymmetric, nonconcerted reaction at the RHF level. However, according to CASSCF results, the  $\pi$ -complex intermediate and its corresponding transition state do not exist. The reaction barrier is estimated to be 4–8 kcal/mol, strongly indicating the existence of the [2+2] products on the Si(001) surface. Of

course, since these calculated reaction barriers are higher than the (zero) [4+2] reaction barrier, one expects the reaction rate of the [4+2] to be much faster than that of the [2+2] reaction at room temperature. The transition state along the symmetric reaction pathway of the [4+2] cycloaddition mechanism is a third-order saddle point with about 4.1 and 0.0 kcal/mol barriers at the MP2//RHF/HW(d) and MCQDPT2//CASSCF(6,6)/HW(d) levels of theory, respectively.

The isomerization from the [2+2] to the [4+2] product involves a substantial barrier of >40 kcal/mol showing that the initial [2+2] reaction products are not converted to [4+2]. In other words, the final reaction products are determined during the initial stage of the reactions implying that the thermodynamics of the reaction products has little to do with the relative distribution of the surface products. This conclusion is in contrast to earlier theoretical<sup>10</sup> and experimental<sup>11</sup> results which suggested that only [4+2] products exist on the Si(001)-(2×1) surface. Therefore, our theoretical results as well as the new experimental study by the Hamers' group<sup>12</sup> are consistent, in that they show that there exists a competition between [4+2] and [2+2] reactions, so that two products are likely to exist on the Si(001) surface.

It has been demonstrated that the newly developed SIMOMM method<sup>13</sup> faithfully reproduces most of the full quantum mechanical results, illustrating that SIMOMM is a useful method in the study of surface chemical reactions, with considerably reduced computational cost. The success of SIMOMM implies that the electronic effects on the surface reaction are highly localized at the surface, and that the effect of the subsurface layers on the surface reaction arises mainly from the geometric constraints. Of course, it must be noted that the SIMOMM method as currently formulated may not be applicable to ionic or metallic surfaces, where high electron delocalization is expected, so one must be careful if applying the method to such cases.

**Acknowledgment.** This work was supported by a DoD CHSSI grant and a grant from the Air Force Office of Scientific Research. The calculations reported here were performed on 14 node and 64 node PC-clusters provided by the Ames Laboratory-USDoE and IBM SP2 obtained via grants from the National Science Foundation and AFOSR. The authors thank Dr. M. Schmidt, Dr. J. Shoemaker, Prof. L. Burggraf, Dr. K. A. Nguyen, and Gordon group members for many helpful discussions.

JA9914285

(26) (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.