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Surface S$_N$2 Reaction by H$_2$O on Chlorinated Si(100)-2 × 1 Surface

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The potential energy surfaces of one, two, and three water molecule sequential adsorptions on the symmetrically chlorinated Si(100)-2 × 1 surface were theoretically explored with SIMOMM:MP2/6-31G(d). The first water molecule adsorption to the surface dimer requires a higher reaction barrier than the subsequent second water molecule adsorption. The lone pair electrons of the incoming water molecule nucleophilically attack the surface Si atom to which the leaving Cl group is bonded, yielding an S$_N$2 type transition state. At the same time, the Cl abstracts the H atom of the incoming water molecule, forming a unique four-membered ring conformation. The second water molecule adsorption to the same surface dimer requires a much lower reaction barrier, which is attributed to the surface cooperative effect by the surface hydroxyl group that can form a hydrogen bond with the incoming second water molecule. The third water molecule adsorption exhibits a higher reaction barrier than the first and the second water molecule adsorption channels but yields a thermodynamically more stable product. In general, it is expected that the surface Si−Cl bonds can be subjected to the substitution reactions by water molecules, yielding surface Si−OH bonds, which can be a good initial template for subsequent surface chemical modifications. However, oversaturations can be a competing side reaction under severe conditions, suggesting that the precise control of surface kinetic environments is necessary to tailor the final surface characteristics.

I. Introduction

Water adsorption on a silicon surface has attracted a great deal of attention due to its potential applications in the semiconductor industry.[1] It is known that an oxide layer (SiO$_2$) grows more easily in the presence of water.[2,3] Therefore, wet oxidation is a preferred choice for the formation of a thick oxide layer. Although it is generally believed that the water undergoes dissociative adsorption on the Si(100) surface, there has been controversy concerning whether the initial adsorption of water is molecular or dissociative. Molecular adsorption (Chart 1a) leaves one surface Si dangling bond intact, while dissociative adsorption (Chart 1b) saturates the surface dangling bonds. Initial interpretations of ultraviolet photoelectron spectroscopy (UPS) on Si(100)[4] and Si(111)[5] suggested molecular adsorption, while electron energy loss spectroscopy (EELS)[6] and surface IR[7] studies showed dissociative adsorption on the basis of the Si−H and Si−O−H stretching modes. Later, photoelectron spectroscopy (PES)[8] reinterpretation of the earlier UPS[8a] data and other experiments[9] were all consistent with dissociative adsorption. At room temperature, the sticking coefficient of water on Si(100) is near unity and constant up to saturation.[10] The saturation coverage is reported to be 0.5 ML: one OH and H per Si dimer.[11]

Konecny and Doren[12] detailed the reaction pathway and the geometries of the product, the transition state, and a molecular precursor state using density functional theory (DFT) and the Si$_9$H$_{12}$ cluster model of the surface. As a water molecule

CHART 1

(a)   (b)
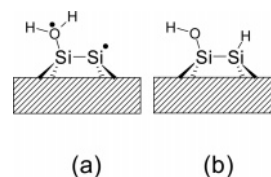
approaches the surface, it finds a molecular precursor state that is about 10 kcal/mol below the reactants, with no intervening reaction barrier. However, MRMP2 results[13] on similar and larger clusters predict the same intermediate to lie 5 kcal/mol below reactants. Cho et al.[14] studied this water adsorption using DFT and a slab model and obtained results that are very similar to those obtained with the DFT cluster models.

The dissociative adsorption inevitably creates a H terminated silicon surface, which is often found to be the main source of slow initial growth rates of oxide films.[15] This phenomenon is called the incubation period effect or substrate-inhibited growth. On the other hand, the surface hydroxyl species have been known to reduce the incubation period in the case of Al$_2$O$_3$ atomic layer deposition (ALD), where the trimethylaluminum (Me$_3$Al) and water are the sources of aluminum and oxygen, respectively.[15a] In addition to this, the surface hydroxyl groups are known to make the film growth more homogeneous[16] than the H terminated Si surface for which island growth is initially prevailing.

Therefore, it is highly desirable to prepare a monolayer of only the hydroxyl group on a Si surface with reasonably good quality. Recently, Lee et al.[17] devised a novel procedure that can create a hydroxyl-only terminated Si surface. The procedure is composed of the chlorination and the subsequent hydroxy-

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lation of the Si surface. However, the detailed reaction mechanisms of the procedure are still unclear.

Chlorine adsorption itself on the Si(100)-2 × 1 surface has been studied extensively.[18,19] It is known that Cl_2 adsorbs dissociatively on the surface and forms a strong polar bond with Si without disrupting the 2 × 1 periodicity. Although a number of reports have attempted to determine the structure of the Cl-covered surface, two different surface model structures have coexisted. The traditional model constitutes two chlorine atoms bonded to the dimer dangling bonds, making a symmetric structure,[18] while the new proposal suggests that only a single chlorine atom is bonded to one of the Si atoms of the surface dimer, making an asymmetric structure.[19] However, recent photoemission experiments concluded that the experimental results are more consistent with the symmetric model.[20]

Due to the highly electronegative chlorine atoms on the Si surface, the water adsorption would be strongly altered as compared to those on a bare Si surface. Therefore, it is of great importance to compare the similarities and the differences of water adsorptions on the two different surfaces. By studying the factors that govern the reactivity of different surfaces, one hopes to gain control over these surface reactions to an extent that eventually leads to a technique to tailor the reaction characteristics.

In this paper, potential energy surface studies of one, two, and three water molecule adsorption mechanisms on a chlorinated surface are systematically performed, adopting the symmetric model of a chlorinated Si(100)-2 × 1 surface as a starting template for the water adsorption.

II. Computational Details

The all-electron 6-31G(d)[21] basis set was used throughout 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). Minima (first-order saddle points) are characterized by Hessians with zero (one) negative eigenvalues. To follow the minimum energy path (MEP), also called the intrinsic reaction coordinate (IRC), the Gonzalez–Schlegel second-order method[22] was used with a step size of 0.3 amu$^{1/2}$-bohr.

The bare surface is inherently multiconfigurational. Therefore, complete active space self-consistent field (CASSCF) wave functions[23] were used to obtain the initial exothermicity of chlorination. A (4,4) active space was designed. It is constructed from the two electrons in the π and $\pi*$ orbitals of the surface Si dimer plus the two electrons in the σ and $\sigma*$ orbitals of the Cl−Cl bond. To recover the dynamic electron correlation, the 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.[24] The particular version of this method used in the present work is referred to as MRMP2 (multireference second-order perturbation theory).[25]

For the study of water adsorption on a chlorinated surface, the MP2 single reference method was used. The general atomic and molecular electronic structure system (GAMESS)[26] program was used for all of the computations.

To study surface size effects, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called surface integrated molecular orbital molecular mechanics (SIMOMM[27]) was used. This approach embeds a smaller QM cluster in a much larger MM cluster in order to reduce or eliminate possible edge
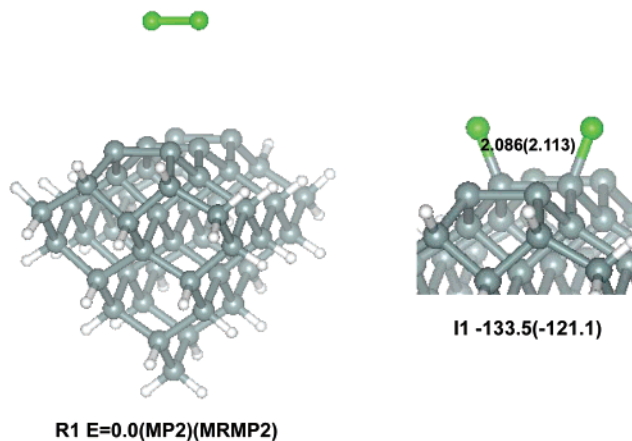

Figure 1. Structural data of the initial reactant and final product of the chlorination reaction in angstroms along with MP2 and MRMP2 energy values in kilocalories per mole. (The number in parentheses is the MRMP2 value).

effects on the (localized) chemistry that occurs on the surface. The SIMOMM models for one, two, and three water molecule adsorptions are composed of $Cl_2OSi_9H_{14}$, $Cl_2O_2Si_9H_{16}$, and $Cl_2O_3Si_9H_{18}$ quantum regions embedded in $Cl_2OSi_{48}H_{38}$, $Cl_2O_2Si_{48}H_{40}$, and $Cl_2O_3Si_{48}H_{42}$ clusters, respectively. MM3[28] 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 Discussions

A. Exothermicity of Symmetric Chlorination. The relative stability of the initial product was calculated with the SIMOMM:MP2/6-31G(d) and SIMOMM:MRMP2(4,4)/6-31G(d) theories in order to understand how the multiconfigurational character of the reactant (bare surface + Cl_2) affects the energetics. These two theories shall be referred to as MP2 and MRMP2, respectively. The initial reactant **R** and the symmetric product **I1** are presented in Figure 1 along with energetic and geometric data. The MP2 theory overestimates the stability of **I1** by 12.5 kcal/mol as compared to the MRMP2 value, indicating that the single reference MP2 theory underestimates the stability of the reactant. The 121.0 kcal/mol of MRMP2 exothermicity could provide large thermal energies to the surface. If the energy relaxation on semiconductor surfaces is not efficient, it is possible that the energy released upon reaction could be converted solely into internal energy of the adsorbate, which would affect subsequent water adsorption reactions.

B. Single Water Molecule Adsorption on a Chlorinated Surface. The potential energy surface of a single water molecule adsorption pathway was explored with SIMOMM:MP2/6-31G-(d), and the results are presented in Figure 2. The reference reactant **R2** is the symmetrically chlorinated surface and H_2O. The intermediate **I2** is initially formed without an intervening reaction barrier. **I2** is stabilized by 6.7 kcal/mol as compared to **R2**, due to the weak interaction between H1 and the electronegative Cl3. Another possible configuration of a weak interaction between O2 and Cl3 was not found. Due to the electronegativity of Cl, it is expected that the surface dimer is positively charged, providing a good environment for the nucleophilic substitution by the incoming O2.

TS1 connects **I2** and another intermediate **I3**, in which O2 is nucleophilically attacking the surface Si4, while Cl3 becomes a leaving group with a reaction barrier of 30.6 kcal/mol, which is 23.9 kcal/mol above the energy of **R2**. The reaction barrier
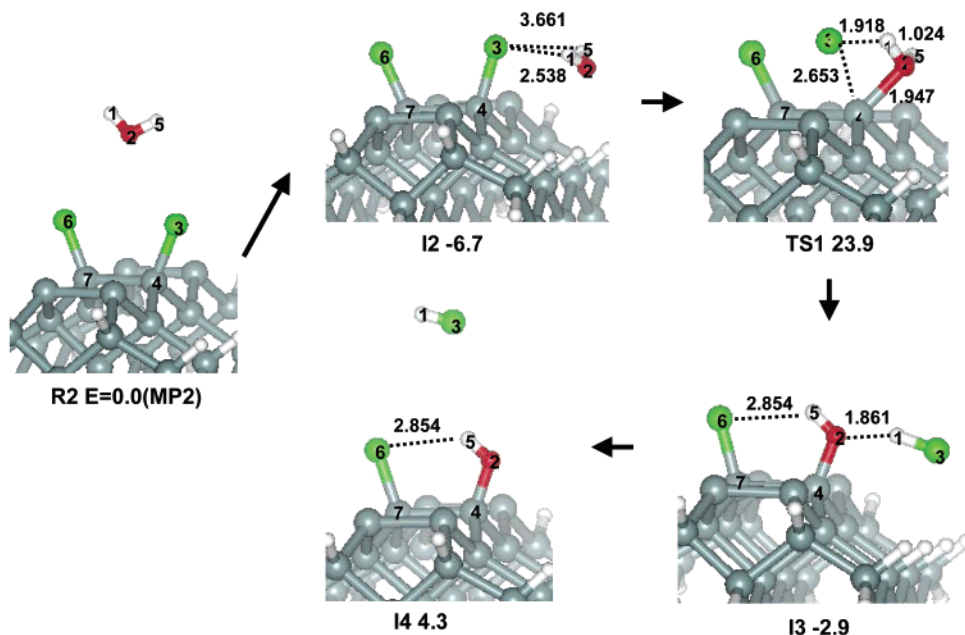
Figure 2. Structural data of the initial reactant, intermediate, transition states, and final product of one water molecule adsorption on the Si(100)-2 × 1 surface in angstroms along with MP2 relative energies in kilocalories per mole.

of **TS1** is somewhat larger than that of other facile surface reactions,[1] but it is not prohibitively large. Therefore, the initial water molecule adsorption reaction on the chlorinated surface is expected to occur, although it may not be facile. Since the leaving group Cl3 is still attached to Si4 in **TS1**, it can be best viewed as an S_N2 type reaction. A unique feature of the current pathway is that the leaving Cl3 is also abstracting H1. Therefore, while the Cl3 is leaving the surface, it is also acting as a base, forming a unique four-membered ring structure (H1−O2−Si4−Cl3) in **TS1**. The H1 of the leaving HCl group forms a hydrogen bond with the O2 of the surface hydroxyl group in the intermediate **I3**. The distance of H1−O2 is calculated to be 1.86 Å, showing a strong bonding interaction. Other than the 7.2 kcal/mol endothermicity, the HCl in **I3** barrierlessly desorbs the surface, yielding the final product **I4**. The reaction is overall 4.3 kcal/mol endothermic.

C. Ring-Closing Reaction of the Mixed Surface. The surface S_N2 reaction by a water molecule yields mixed Si−Cl and Si−OH on the surface dimer, as shown in **R3** (see Figure 3). The O2 of the hydroxyl group has lone pair electrons that can act as a nucleophile to the electron deficient Si4. Therefore, the ring-closing reaction can occur. **TS2** connecting **R3** and the ring-closed intermediate **I5** was located with a forward reaction barrier of 70.9 kcal/mol, effectively prohibiting the thermal ring-closing reaction. As in **TS1**, the S_N2 reaction and the hydrogen abstraction by leaving Cl occur at the same time. The HCl molecule is still making a hydrogen bond with the surface oxygen in the intermediate **I5**, which is less stable than the reactant **R3** by 53.2 kcal/mol. Therefore, **I5** is kinetically hardly accessible and thermodynamically very unstable. The desorption of the attached HCl in **I5** requires 9.3 kcal/mol. The final product **I6** is 62.5 kcal/mol above the energy of **R3**. According to these theoretical results, it is clear that the ring-closing reaction would not easily occur. No sign of product **I6** was found in the experiment.[17]

D. The Second Water Molecule Adsorption. As the water adsorption proceeds, more than one water molecule can adsorb on the surface dimer. The first water molecule adsorbed surface has both Si−Cl and Si−OH, as shown in **R4** (see Figure 4). The surface conformation of **R4** is slightly different from that
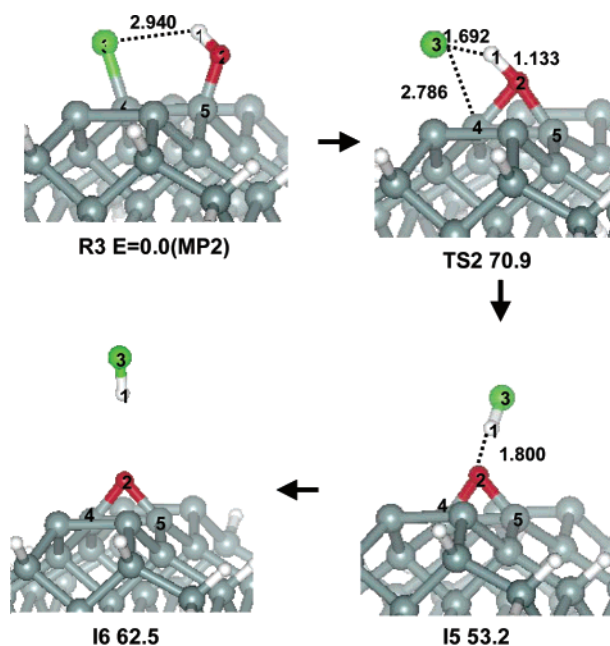

Figure 3. Structural data of the initial reactant, intermediate, transition states, and final product of the ring-closing reaction on the Si(100)-2 × 1 surface in angstroms along with MP2 relative energies in kilocalories per mole.

of **R3**, in which interaction between H1−Cl6 exists. According to our calculation, this interaction stabilizes **R3** by 1.5 kcal/mol as compared to **R4**. Therefore, it is expected that the two conformational isomers can both exist on the surface with the slight preference of **R3**. Our potential energy surface study of the second water molecule adsorption yielded two different reaction channels depending on the pathways of the second water molecule that can approach either to the surface hydroxyl group or to the surface Cl. However, both channels lead to the same final product. Regardless of the initial surface conformers used (**R3** and **R4**), the former approach yielded two different initial intermediates, **I7** and **I8**, which are more stable then **R4** by 12.3 and 15.3 kcal/mol, respectively. Except the exothermicities of **I7** and **I8**, they are formed without a reaction barrier.
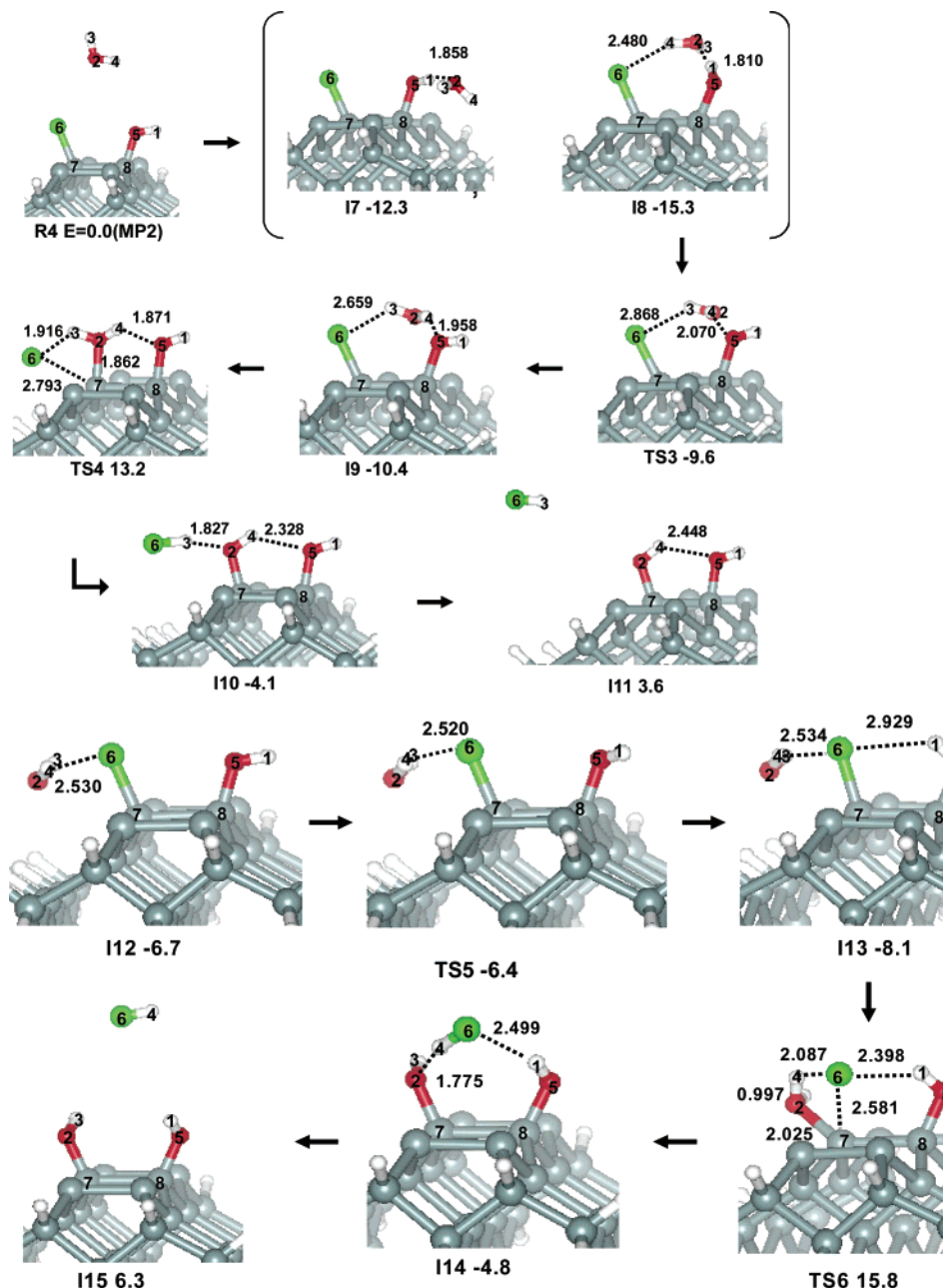
Figure 4. Structural data of the initial reactant, intermediate, transition states, and final product of the second water molecule adsorption on the Si(100)-2 × 1 surface in angstroms along with MP2 relative energies in kilocalories per mole.

Due to the flat potential energy surface, a transition state connecting **I7** and **I8** was not found. **I7** needs to isomerize to **I8** for the subsequent reaction to occur. In both of the **I7** and **I8** intermediates, the O2 of the incoming water molecule is hydrogen-bonded to the surface H1. However, in order for O2 to act as a nucleophile, H1−O2 needs to be broken. The transitions state **TS3** connecting **I8** and **I9** is found where the H1−O2 hydrogen bonding is being broken and H4−O5 hydrogen bonding is being formed with a reaction barrier of 5.7 kcal/mol. However, **TS3** is an internal barrier, since it is more stable than **R4** by 9.6 kcal/mol. The O2 of the incoming water molecule is now ready to nucleophilically interact with the Si7. The transition state **TS4** connecting **I9** and another intermediate **I10** was located with a reaction barrier of 23.6 kcal/mol (13.2 kcal/mol above the energy of **R4**). The same as **TS1**, an S$_N$2 reaction by the O2 and a hydrogen abstraction by Cl6 occur at the same time in **TS4**. However, additional H4−O5 hydrogen bonding appears in **TS4** which is absent in **TS1**. This

extra cooperative effect can explain the overall 10.7 kcal/mol energy reduction of **TS4** relative to **TS1**. Therefore, it is clear that the secondary water molecule adsorption requires a much lower reaction energy than the first water molecule adsorption. The leaving HCl molecule forms a hydrogen bond in **I10**. Except the overall endothermicity of 3.6 kcal/mol, the HCl leaves the surface without any intervening reaction barrier, yielding the final product **I11**. It is noted that the internal hydrogen bonding of O5−H4 exists in **I11**, which stabilizes the surface hydroxyl groups.

The water approaches Cl6 in the second possible channel of the secondary water molecule adsorption, as shown in **I12**, where the H4 of the incoming water molecule forms a weak interaction with Cl6. It is more stable than **R4** by −6.7 kcal/mol. (Note that the **R4** surface conformer was used initially rather than **R3**.) A mild transition state **TS5** connects **I12** and **I13**, where the H1 is interacting with the Cl6. The intermediate **I13** can be considered as the initial surface intermediate, if the
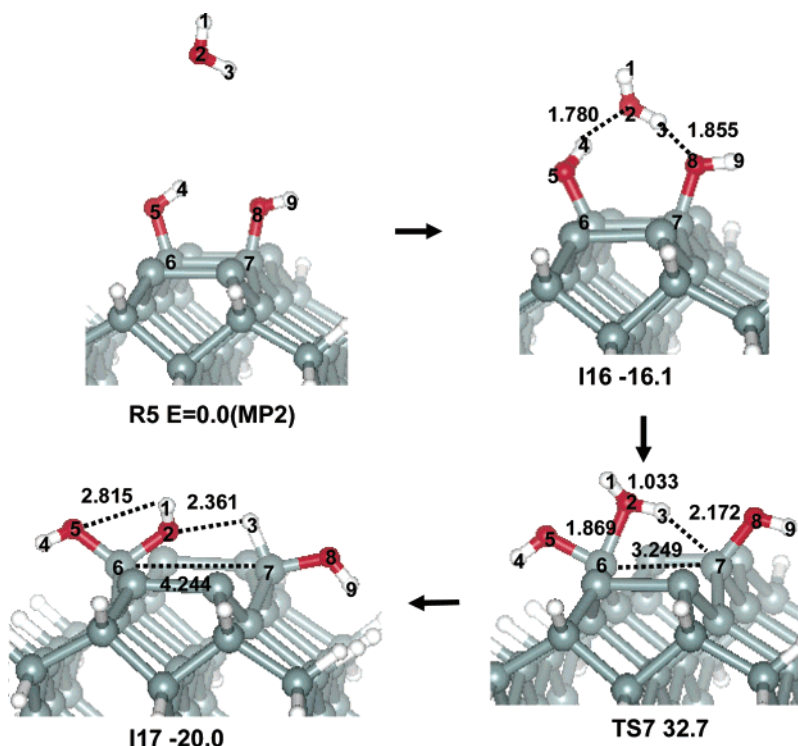
Figure 5. Structural data of the initial reactant, intermediate, transition states, and final product of the third water molecule adsorption on the Si(100)-2 × 1 surface in angstroms along with MP2 relative energies in kilocalories per mole.

R3 surface conformer was initially used. The isomerization from **I12** to **I13** is necessary for the subsequent reaction to occur. The transition state **TS6** connecting **I13** and another intermediate **I14** was found with a reaction barrier of 23.9 kcal/mol. It is 15.8 kcal/mol above the energy of **R4**, which is 2.6 kcal/mol higher than that of **TS4** but is 8.1 kcal/mol lower than that of **TS1**. As in **TS4**, an S_N2 type reaction by O2 and a H4 abstraction by Cl6 occur at the same time. However, unlike **TS4** where H4−O5 hydrogen bonding stabilizes the transition state, a weak interaction between H1−Cl6 exists in **TS6**. Again, except an overall endothermicity of 6.3 kcal/mol, the HCl leaves the surface without reaction barriers from the intermediate **I14**.

The two channels described in this section eventually lead to the same surface product, in which the surface dimer is saturated only with hydroxyl groups (see **I11** and **I15**). However, while the former channel naturally leads to the hydrogen-bonded conformer **I11**, the latter channel leads to no hydrogen-bonded conformer **I15**. The O5−H4 hydrogen bonding stabilizes **I11** relative to **I15** by 2.7 kcal/mol. These two final conformers are expected to coexist. Both channels have much lower reaction barriers as compared to the first water molecule adsorption due to the surface cooperative effects. Therefore, once the initial water molecule adsorption occurs, the subsequent water adsorptions would occur relatively easily. These two water molecule adsorptions yielded a hydroxyl-group-only terminated surface dimer, which can provide an excellent reaction environment for the subsequent surface chemical modifications.

E. The Third Water Molecule Adsorption. It is possible that another water molecule can adsorb on the hydroxyl saturated surface **R5** (see Figure 5, note that the **I11** surface conformer which has hydrogen bonding was used rather than the **I15** conformer). The doubly hydrogen-bonded structure **I16** was found with a 16.1 kcal/mol stabilization energy as compared to **R5**. The transition state **TS7** connects **I16** and the final product **I17** with a 48.8 kcal/mol reaction barrier. It is 32.7 kcal/mol above the energy of **R5**, which is still much higher than the first and secondary water molecule adsorption reactions. There-
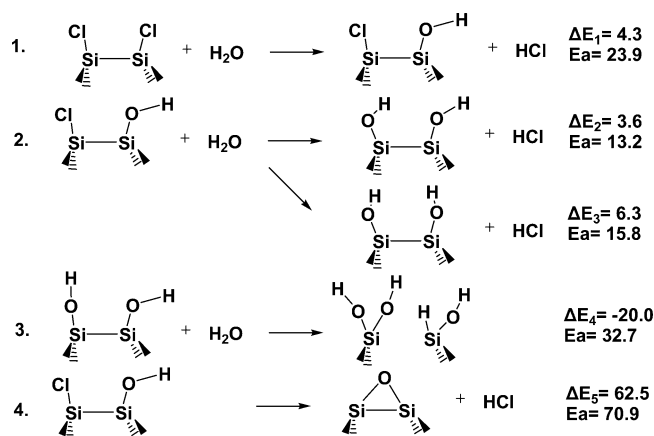

Figure 6. Overall thermodynamic and kinetic data of individual reaction channels in kilocalories per mole.

fore, this channel can be only accessible in the more severe environments. The O2 nucleophilically attacks the Si6 in the **TS7**. As a result, the Si7 becomes the leaving group. The Si7 also abstracts the H3 of the incoming water molecule. As a result of this complex transition state, the incoming water molecule dissociatively adsorbs on the surface, as shown in **I17**, where the O2−H3 chemical bond becomes the O2−H3 hydrogen bond. The final product **I17** is stabilized by 20 kcal/mol as compared to the **R5**. Therefore, unlike the one and two water molecule adsorptions, dissociatively inserting a third water molecule into the surface Si−Si σ bond is thermodynamically quite favorable. Although it is a minor product, a signature of surface Si atom that is bonded with two O atoms appeared in the experimental data.[17]

F. Thermodynamic Aspects. The initial experimental reaction environment would be under nonequilibrium conditions. Therefore, the surface reactions are more affected by the kinetic factors rather than the thermodynamic ones. Nonetheless, the thermodynamic data are important to understand the thermal

relaxations of the reacted surface. The overall thermodynamic data of each individual reaction channel are presented in Figure 6. While one and two water molecule adsorption reactions are slightly endothermic by 3.6–6.3 kcal/mol, the third water molecule adsorption is exothermic by 20 kcal/mol. Therefore, if these three reactions are combined, the overall three water molecule adsorption reaction becomes 12.1 kcal/mol exothermic. The surface ring-closing reaction is 62.5 kcal/mol endothermic, showing that it is thermodynamically highly unstable. Therefore, it would not be an important structure. However, if this is coupled with the highly exothermic chlorination step, such an energetically unstable surface species can have a chance to exist.

IV. Conclusions

The potential energy surfaces of one, two, and three water molecule sequential adsorptions on the symmetric chlorinated surface were theoretically explored with SIMOMM:MP2/6-31G-(d). One water molecule adsorption on the chlorinated surface dimer requires a 23.9 kcal/mol overall reaction energy. It is somewhat larger than other facile chemical reactions, although it is not prohibitively large. According to our reaction mechanism studies, the lone pair electrons of the incoming water molecule nucleophilically attack the surface Si atom to which the Cl is bonded, yielding an S_N2 type transition state. At the same time, the Cl abstracts the H atom of the incoming water molecule, forming a unique four-membered ring conformation. A subsequent ring-closing reaction of the one water molecule adsorbed surface would not easily occur due to the high reaction barrier. Two reaction channels are found for the second water molecule adsorption on the one water molecule adsorbed surface dimer. The overall reaction energies are calculated to be 13.2 and 15.8 kcal/mol, respectively. These numbers are very close to the experimental value 12.9 kcal/mol.[17] They are much lower than that of the first water molecule adsorption. The reductions of the reaction barriers were attributed to the cooperative effect of already adsorbed surface species through the hydrogen bonding. The third water molecule adsorption exhibits higher reaction energies of 32.7 kcal/mol but yields thermodynamically the most stable product. Experimentally, the surface Si that is bonded with two O atoms was observed,[17] suggesting the possibilities of these three water molecule adsorbed products.

In general, it is expected that the Si–Cl bonds of the chlorinated surface can be replaced by a hydroxyl group, which is a good initial template for the subsequent surface chemical modifications, substantiating the recent experimental results.[17] Side reactions such as the surface ring-closing reaction would not easily occur due to its large reaction barriers. However, the oversaturation of three water molecule adsorption can occur, showing that precise control of the surface kinetic environments is necessary to tailor the final surface characteristics. As a first step toward establishing techniques to control the surface chemical reactions, the chlorinated surface provides promising new testing grounds.

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