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Citation: *J. Chem. Phys.* **135**, 244707 (2011); doi: 10.1063/1.3671454

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# Adsorption mechanisms of isoxazole and oxazole on Si(100)-2 × 1 surface: Si–N dative bond addition vs. [4+2] cycloaddition

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(Received 8 September 2011; accepted 29 November 2011; published online 28 December 2011)

The surface reaction pathways of isoxazole and oxazole on Si(100)-2 × 1 surface were theoretically investigated. They both form a weakly bound Si–N dative bond adduct on Si(100)-2 × 1 surface. In the case of isoxazole, the barrierlessly formed Si–N adduct is the most important surface product, that cannot be easily converted into other species. On the other hand, a facile concerted [4+2]<sub>CC</sub> cycloaddition without involving the initial Si–N dative bond adduct was also found in the case of oxazole adsorption. The existence of Diels-Alder reactions is attributed to the particular arrangement of the two heteroatoms of oxazole in such a way that the two Si–C  $\sigma$ -bonds can be formed in a [4+2] fashion. In short, the unique geometric arrangements and electronegativity of these similar heteroatomic molecules yielded distinctively different surface reaction characteristics. © 2011 American Institute of Physics. [doi:10.1063/1.3671454]

## I. INTRODUCTIONS

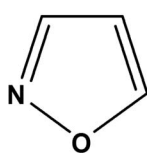
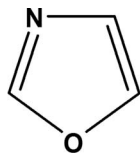
Cycloaddition reaction has been a very important class of surface reactions on semiconductor silicon surface.<sup>1</sup> Although the direct addition of a single C=C  $\pi$  bond to the Si dimer on the Si(100) surface constitutes the orbital symmetry forbidden 2s+2s cycloaddition,<sup>2</sup> early experimental,<sup>3</sup> and theoretical<sup>4</sup> studies have shown that the unsaturated hydrocarbons, such as acetylene, ethylene, and propylene can readily react with Si(100) surface yielding [2+2] products. However, there has been a controversy<sup>5</sup> over the stereochemistry of the reactions. The two most likely reaction pathways of alkene adsorption are a  $\pi$ -complex and a diradical channels. The  $\pi$ -complex channel can be described by a three-atom intermediate, in which the stereochemistry should be retained as the alkene approaches to the Si dimer. Therefore, the  $\pi$ -complex channel is stereospecific. On the other hand, the diradical channel can be described by a Si–C single-bonded diradical intermediate. Once the alkene  $\pi$ -bond is broken, rotation around the C–C  $\sigma$ -bond is possible, resulting in a loss of stereospecificity, if it occurs before the second Si–C bond is formed. According to a comparative theoretical study<sup>6</sup> of the adsorptions of ethylene and 2-butene on Si(100), both the diradical and the  $\pi$ -complex pathway were found. Since the net reaction barriers of the channels are similar, it was concluded that the final distributions of surface products may depend on the experimental kinetic environment as well as substituents. In any event, these diradical and  $\pi$ -complex channels of [2+2] cycloadditions constitute an asymmetric stepwise path.

Diene systems have also been actively studied. Pioneering theoretical and experimental studies have shown<sup>7</sup> that the surface dimer can act as a good dienophile yielding “Diels-Alder”-like [4+2] cycloaddition products, in which a conju-

gated diene reacts with the silicon surface dimer to form a six-membered ring. In a subsequent experiment by Hamers and co-workers<sup>8</sup> supported the observation. However, they noted a minor [2+2] product as well, strongly indicating the existence of competition between [4+2] and [2+2] reactions in the adsorption of diene on the Si(100) surface. Theoretical studies by Choi and Gordon<sup>9</sup> support for the existence of competing reactions by showing that there exists a low energy [2+2] cycloaddition pathway in addition to the [4+2] path. They also showed that the [4+2] channel is concerted contrasting to the stepwise path of [2+2]. Cycloaddition can also be found in the adsorptions of aromatic molecules. The aromatic benzene<sup>10</sup> can easily adsorb on Si(100) surface via concerted [4+2] path. Theoretical study on benzene adsorption with multireference methods<sup>10</sup> showed that although the [4+2], [2+2], and tetra- $\sigma$ -bonded products are possible, the [4+2] product is thermodynamically the most stable and kinetically the most easily accessible. Unlike conjugated dienes, it appears that benzene selectively prefers [4+2] cycloaddition reaction on the Si(100) surface.

It is interesting to note that the mechanism of [4+2] cycloaddition can be significantly altered when substituents are introduced. In the theoretical study of acrylonitrile on the Si(100)-2 × 1 surface,<sup>11</sup> it was reported that a stepwise [4+2] types of reaction occurs by way of dative bond intermediate in which the nitrogen lone pair of acrylonitrile initially forms a stable bond with the surface Si dimer. The stepwise [4+2] channel can also be implied in the case of pyridine adsorption on Si(100). On the basis of thermal desorption spectroscopy, XPS, high-resolution electron energy loss spectroscopy, and density functional theory (DFT) calculations,<sup>12</sup> the dative-bonded pyridine through the lone pair electrons of N and [4+2]-like cycloadduct with two  $\sigma$ -linkages of Si–N and Si–C on Si(100) were reported. The latter product implies a stepwise path of [4+2] addition, since one of the  $\sigma$ -linkages is Si–N bond. It was shown that the adsorptions of aromatic

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**Isoxazole****Oxazole**

SCHEME 1.

isoxazole<sup>13</sup> on Si(111) surface yield dative bond addition and [4+2]-like cycloaddition. On the other hand, the adsorptions of oxazole on the same surface yield dative bond addition and [2+2]-like cycloaddition. All of these products contain one Si–N surface bond indicating that they share the same dative bond intermediate in their reaction mechanisms. These studies on heterogeneous aromatic systems inherently assume that the overall reactions are stepwise and dative bond formation precedes cycloadditions. So the cycloaddition reactions only occur afterwards, implying no direction reaction competition between the dative addition and the cycloaddition. However, the concerted [4+2] cycloaddition is well known to have very small or near zero reaction barriers. Therefore, in some particular conditions, the concerted [4+2] cycloaddition can be directly formed without the dative-bonded precursor state. Theoretical mechanism study can be helpful to clarify this.

Unlike common conjugated molecules, isoxazole and oxazole (Scheme 1) show considerable aromaticity; also unlike benzene, it has inhomogeneous electron distribution and two heteroatoms with lone pair electrons. For formulation of an aromatic  $\pi$  conjugation of  $4n + 2$  electrons, the oxygen atom and nitrogen atom contribute two and one electrons, respectively. Because these molecules contain both an aromatic ring and lone pair electrons, the molecules are expected to form a variety of adsorption states with silicon surface via either cycloaddition reaction or dative bonding Lewis base-acid reaction. In this paper, the initial potential energy surfaces of isoxazole and oxazole on Si(100)-2  $\times$  1 surface were theo-

retically explored to understand the effects of the particular heteroatom arrangements on their surface reaction characteristics.

## II. COMPUTATIONAL DETAILS

All electron 6-31G(d) (Ref. 14) basis set was used throughout this work. Minimum energy reaction paths were determined by first optimizing the geometries of minima and transition states. Then each stationary point was characterized by computing and diagonalizing the Hessian matrix (matrix of energy second derivatives). Various points on the reaction paths, particularly transition states and intermediates, are often inherently multiconfiguration especially in the case of cycloadditions. Therefore, complete active space self-consistent field (CASSCF) wave functions<sup>15</sup> were used to describe entire potential energy surfaces. For the study of adsorption and chemisorption of isoxazole and oxazole on the Si(100)-2  $\times$  1 surface, individual sets of active spaces were used for each channels shown in Table I.

In order 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.<sup>16</sup> The particular version of this method used in the present work is referred to as multireference second-order perturbation theory (MRMP2).<sup>17</sup> The relative energies will focus on the MRMP2 values obtained at the multi-configurational self-consistent field (MCSCF) geometries (MRMP2/MCSCF). The general atomic and molecular electronic structure system<sup>18</sup> program was used for all of the computations.

In order to include surface size effects, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called surface integrated molecular orbital molecular mechanics (SIMOMM) (Ref. 19) was adopted. In this work, the QM/MM models were designed such that C<sub>3</sub>NOSi<sub>9</sub>H<sub>15</sub> quantum region embedded in C<sub>3</sub>NOSi<sub>48</sub>H<sub>39</sub> cluster, for both oxazole and isoxazole. All figures show only the QM region for clarity. The

TABLE I. Design of CASSCF active spaces of various reaction channels.

Reaction channel	Active space size	Construction
Exchange between Si–N and Si–O dative-bonded intermediate in isoxazole (Figure 1)	(8,5)	Two electrons in the $\pi$ and $\pi^*$ orbitals of surface Si dimer + two electrons in the one nonbonding orbitals of nitrogen + four electrons in the two nonbonding orbitals of oxygen.
[2+2] <sub>NC</sub> cycloaddition reaction (Figures 2 and 3)	(6,5)	Two electrons in the $\pi$ and $\pi^*$ orbitals of surface Si dimer + two electrons in the $\pi$ and $\pi^*$ orbitals of N = C bond + two electrons in the one nonbonding orbitals of nitrogen.
[2+2] <sub>CC</sub> cycloaddition reaction (Figures 4 and 5)	(4,4)	Two electrons in the $\pi$ and $\pi^*$ orbitals of surface Si dimer + two electrons in the $\pi$ and $\pi^*$ orbitals of C = C bond.
[4+2] cycloaddition reaction (Figures 6 and 7)	(8,7)	Two electrons in the $\pi$ and $\pi^*$ orbitals of surface Si dimer + two electrons in the $\pi$ and $\pi^*$ orbitals of N = C bond + two electrons in the $\pi$ and $\pi^*$ orbitals of C = C bond + two electrons in the one nonbonding orbitals of nitrogen.
Ring-opening reaction of isoxazole (Figure 8)	(10,7)	Two electrons in the $\pi$ and $\pi^*$ orbitals of surface Si dimer + two electrons in the $\sigma$ and $\sigma^*$ orbitals of N–O bond + two electrons in the one nonbonding orbitals of nitrogen + four electrons in the two nonbonding orbitals of oxygen.

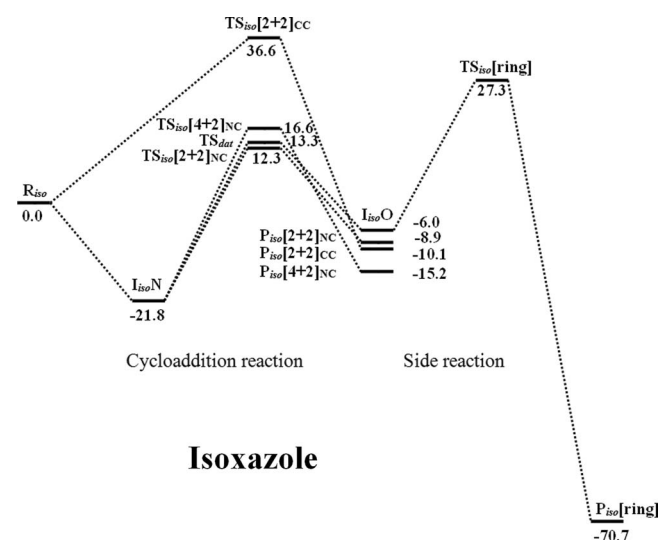
chemically inactive region of the system is calculated by computationally inexpensive force field methods, while the chemically active part is treated by quantum mechanics. It has been shown that the SIMOMM (surface integrated molecular orbital molecular mechanics) QM/MM method gives reasonable results at relatively low computational cost.<sup>1</sup> The SIMOMM method has been used successfully to study many different adsorbates on Si(100)-2 × 1 surface,<sup>20</sup> as well as the Si(111)-7 × 7 reconstructed surface,<sup>21</sup> the SiC(100) surface,<sup>22</sup> and the diamond(100) surface.<sup>23</sup> MM3 (Ref. 24) parameters were used for the molecular mechanics part of the computations. All of the computations were done without imposing symmetry unless otherwise specified.

### III. RESULTS AND DISCUSSIONS

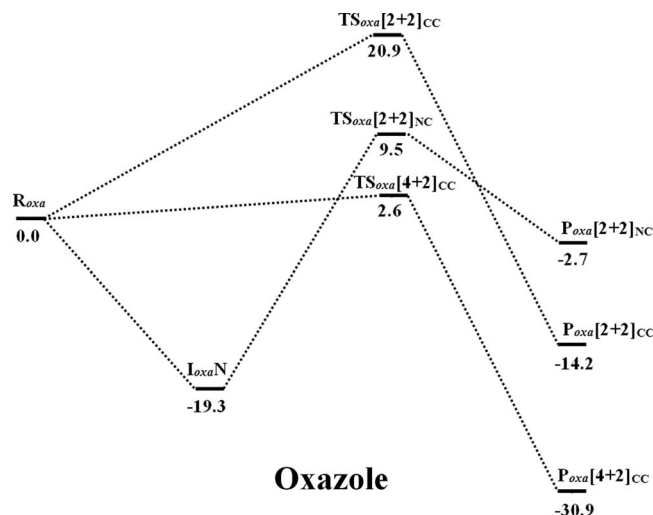
Due to the two heteroatoms of oxazole and isoxazole, several surface binding configurations are possible. According to our calculations, a Si–N as well as a Si–O dative bond adducts were found. In the case of cycloadditions, [2+2]<sub>NC</sub>, [2+2]<sub>CC</sub>, [4+2]<sub>NC</sub> and [4+2]<sub>CC</sub> products were found, where the subscript NC represents that one of the surface  $\sigma$ -bond is Si–N. The subscript CC emphasizes Si–C only surface  $\sigma$ -bonds. In all figures grey, red, blue, and white colored atoms represent C, O, N, and H, respectively. The overall energetics along the potential energy surfaces for isoxazole and oxazole are collected in Schemes 2 and 3. All notations of R, I, TS, and P in figures correspond to reactant, intermediate, transition state, and product, respectively.

#### A. Dative bonded adducts

As in the cases of the pyridine,<sup>12</sup> pyrazine,<sup>25</sup> and 1-pyrazoline,<sup>26</sup> the N–Si dative-bonded adducts were found in the initial adsorptions of isoxazole and oxazole on the Si(100)-2 × 1 surface (see Figures 1 and 2). They are represented in the figures as  $I_{iso}N$  and  $I_{oxa}N$ , respectively. This end-on chemisorption occurs barrierlessly through a



SCHEME 2. The potential energy surfaces (PES) along the cycloaddition and side reactions of isoxazole.



SCHEME 3. The potential energy surfaces (PES) along the cycloaddition reactions of oxazole.

nucleophilic attack of the N lone pairs to the positively charged Si atom of the surface dimer. The stabilization energies of these Si–N dative-bonded adduct species are 21.8 and 19.3 kcal/mol for  $I_{iso}N$  and  $I_{oxa}N$ , respectively, at the MRMP2//CASSCF(8,5)/6-31G(d) level of theory. These values are in good agreements with those of pyridine,<sup>12</sup> pyrazine, and 1-pyrazoline.<sup>26</sup>

In addition to Si–N bonded adduct, Si–O dative bond adduct  $I_{iso}O$  has been also observed in isoxazole adsorption (see Figure 1). Although it is less stable than Si–N adduct ( $I_{iso}N$ ) by 15.8 kcal/mol, its formation is exothermic by 6.0 kcal/mol relative to the reactants. The same chemisorption state (Si–O dative bond) also has been observed in the case of furan<sup>27,28</sup> adsorbed on the Si(100) surface with the similar stabilization energy. The isomerization between Si–N adduct ( $I_{iso}N$ ) and Si–O adduct ( $I_{iso}O$ ) occurs through the transition state  $TS_{dat}$ , in which both of the Si<sub>6</sub>–N<sub>2</sub> and Si<sub>6</sub>–O<sub>1</sub> bond lengths are elongated by 1.331 and 0.937 Å than those of the dative bonded intermediates  $I_{iso}N$  and  $I_{iso}O$ , respectively. So the  $TS_{dat}$  constitutes a  $\pi$ -complex configuration. The reaction barrier of  $TS_{dat}$  is calculated to be 13.3 kcal/mol at the MRMP2//CASSCF(8,5)/6-31G(d) level of theory. Since the isomerization barrier is not too much high, Si–O adduct has a chance to exist. However, the Si–O adduct is energetically less stable than Si–N adduct. So the Si–N adduct is more important initial surface species. The same chemisorption state (Si–O dative bond) has not been observed in the case of oxazole.

#### B. Direct and indirect [2+2] cycloaddition reaction channels

One of the main issues is whether the cycloaddition occurs as a subsequent surface reaction from the Si–N dative adducts or it occurs directly without it. According to our calculations, both channels are possible.

**Stepwise Mechanism of [2+2]<sub>NC</sub> Products:** In both of the isoxazole and oxazole, the [2+2]<sub>NC</sub> products are formed by way of Si–N dative bond adducts



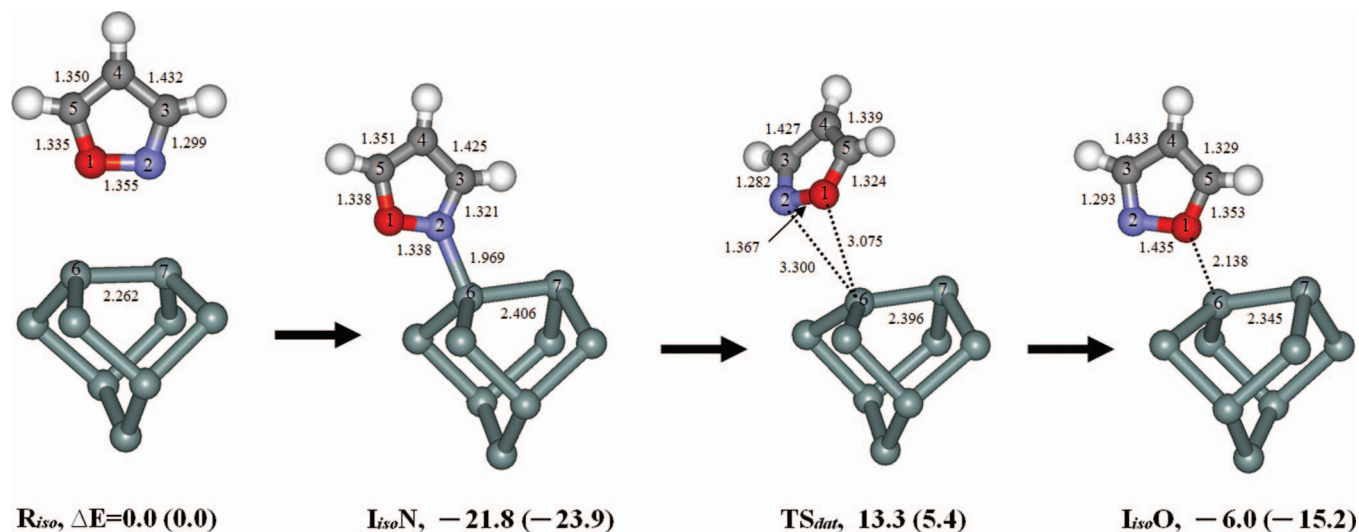


FIG. 1. The CASSCF transition states and intermediates along the Si-N and Si-O dative bond exchange channel of isoxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

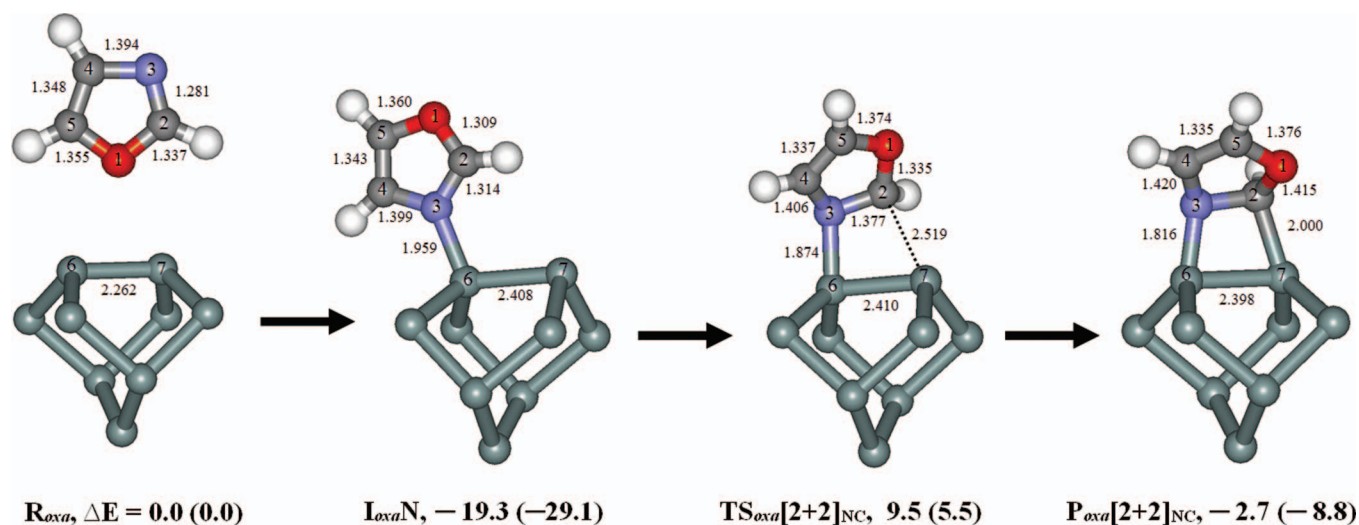


FIG. 2. The CASSCF transition states and intermediates along the  $[2+2]_{CN}$  cycloaddition channel of oxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

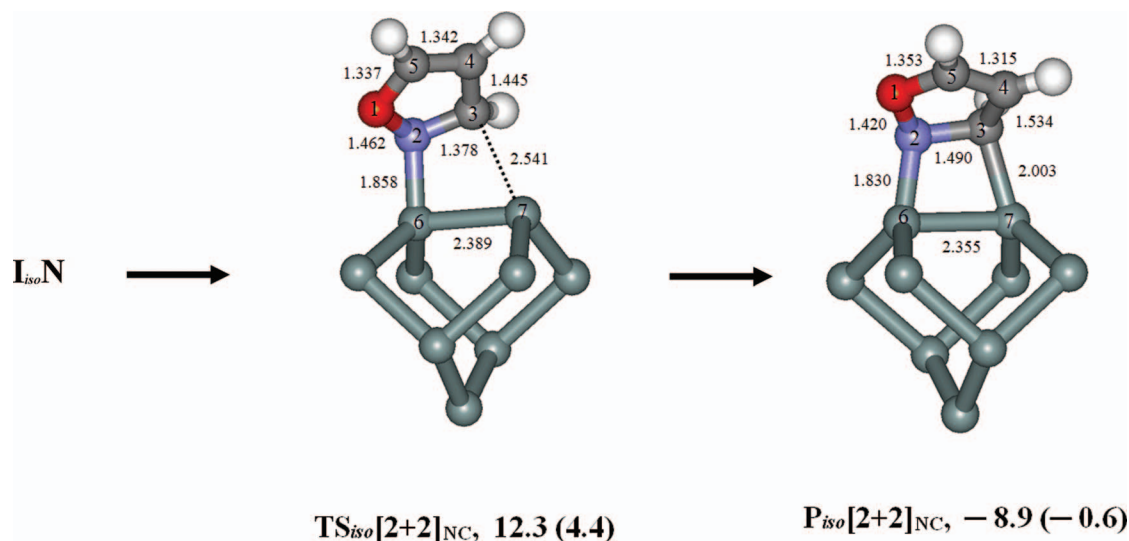


FIG. 3. The CASSCF transition states and intermediates along the  $[2+2]_{CN}$  cycloaddition channel of isoxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

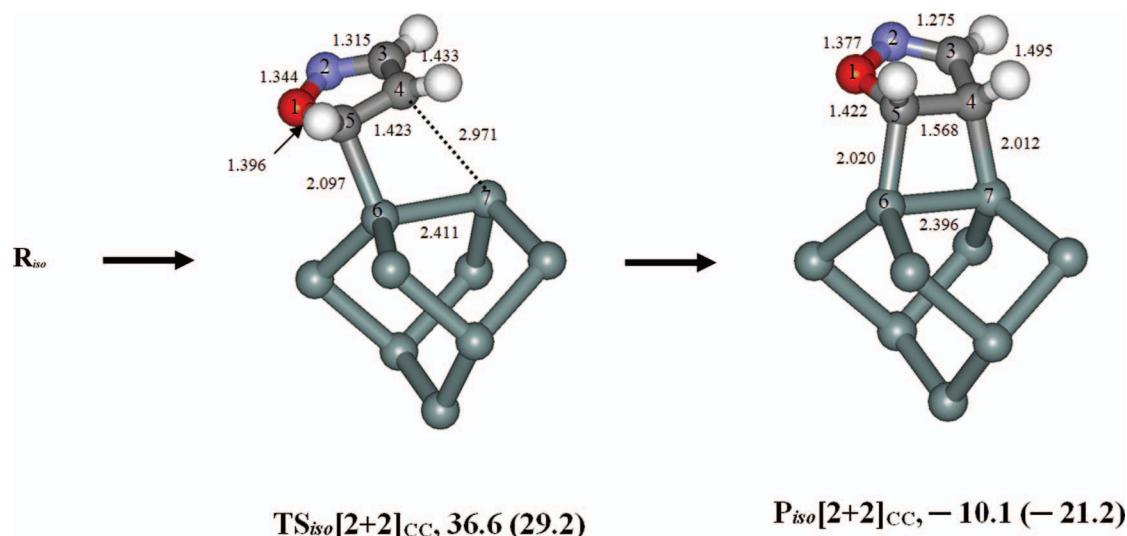


FIG. 4. The CASSCF transition states and intermediates along the  $[2+2]_{CC}$  cycloaddition channel of isoxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

constituting a stepwise  $[2+2]$  cycloaddition mechanism between the  $\text{N}=\text{C}$  double bond and the surface  $\text{Si}=\text{Si}$  dimer. In the case of isoxazole (see Figure 3), the  $[2+2]$  transition state ( $\text{TS}_{iso}[2+2]_{NC}$ ) connects the stable  $\text{Si}-\text{N}$  adduct ( $\text{I}_{iso}\text{N}$ ) and the  $[2+2]_{NC}$  product ( $\text{P}_{iso}[2+2]_{NC}$ ) with the reaction barrier of 12.3 kcal/mol. This  $[2+2]_{NC}$  reaction barrier is 1.0 kcal/mol lower than that of isomerization to the  $\text{Si}-\text{O}$  adduct and the finally formed  $[2+2]_{NC}$  product ( $\text{P}_{iso}[2+2]_{NC}$ ) is more stable than the  $\text{Si}-\text{O}$  adduct by 2.9 kcal/mol. Therefore,  $[2+2]_{NC}$  product ( $\text{P}_{iso}[2+2]_{NC}$ ) is slightly more favorable than the  $\text{Si}-\text{O}$  adduct ( $\text{I}_{iso}\text{O}$ ) both kinetically and thermodynamically. The similar stepwise reaction to  $[2+2]_{NC}$  product ( $\text{P}_{oxa}[2+2]_{NC}$ ) is also found in the case of oxazole (see Figure 2). The asymmetric transition state ( $\text{TS}_{oxa}[2+2]_{NC}$ ) connects the initial  $\text{Si}-\text{N}$  adduct ( $\text{I}_{oxa}\text{N}$ ) and the  $[2+2]_{NC}$

product ( $\text{P}_{oxa}[2+2]_{NC}$ ) with the barrier height of 9.5 kcal/mol. It is 2.8 kcal/mol lower than  $\text{TS}_{iso}[2+2]_{NC}$  (see Schemes 2 and 3). However, the final  $[2+2]_{NC}$  product ( $\text{P}_{oxa}[2+2]_{NC}$ ) is just 2.7 kcal/mol exothermic. In short, although the  $[2+2]_{NC}$  of oxazole is kinetically more easily accessible than that of isoxazole, it is thermodynamically less favorable.

**Concerted Mechanism of  $[2+2]_{CC}$  Products:** The  $[2+2]_{CC}$  is the cycloaddition product between the  $\text{C}=\text{C}$  of molecules and the surface  $\text{Si}=\text{Si}$  dimer. Since it does not involve the nitrogen, the  $[2+2]_{CC}$  is formed directly without the precursor state of  $\text{Si}-\text{N}$  dative adduct. In the case of isoxazole, the transition state ( $\text{TS}_{iso}[2+2]_{CC}$ ) directly connects the reactants and the  $[2+2]_{CC}$  product ( $\text{P}_{iso}[2+2]_{CC}$ ) (see Figure 4). The reaction barrier of this path is 36.6 kcal/mol,

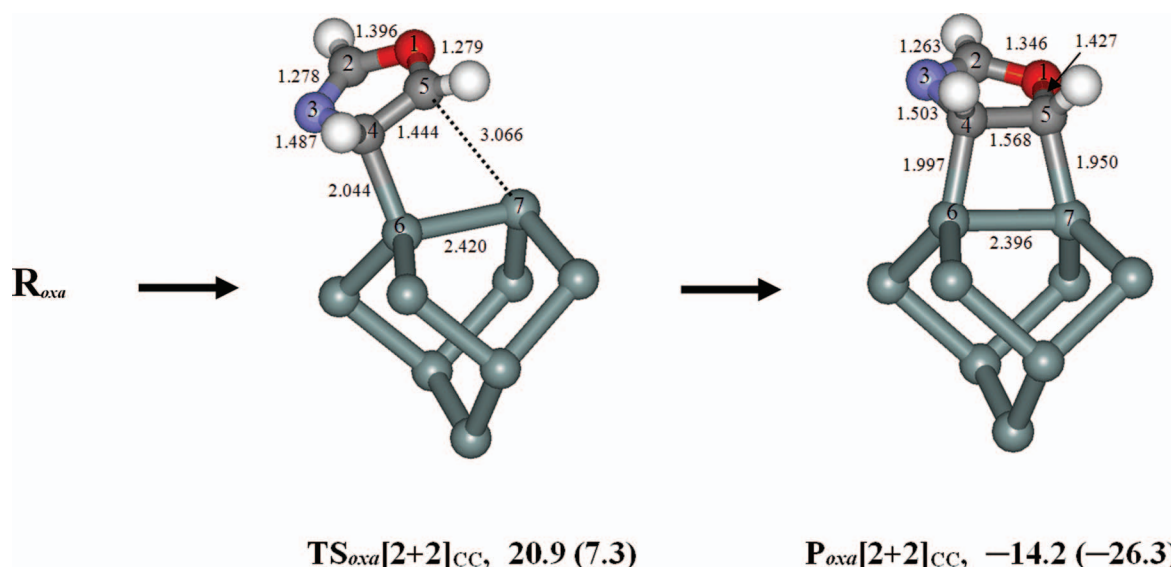


FIG. 5. The CASSCF transition states and intermediates along the  $[2+2]_{CC}$  cycloaddition channel of oxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

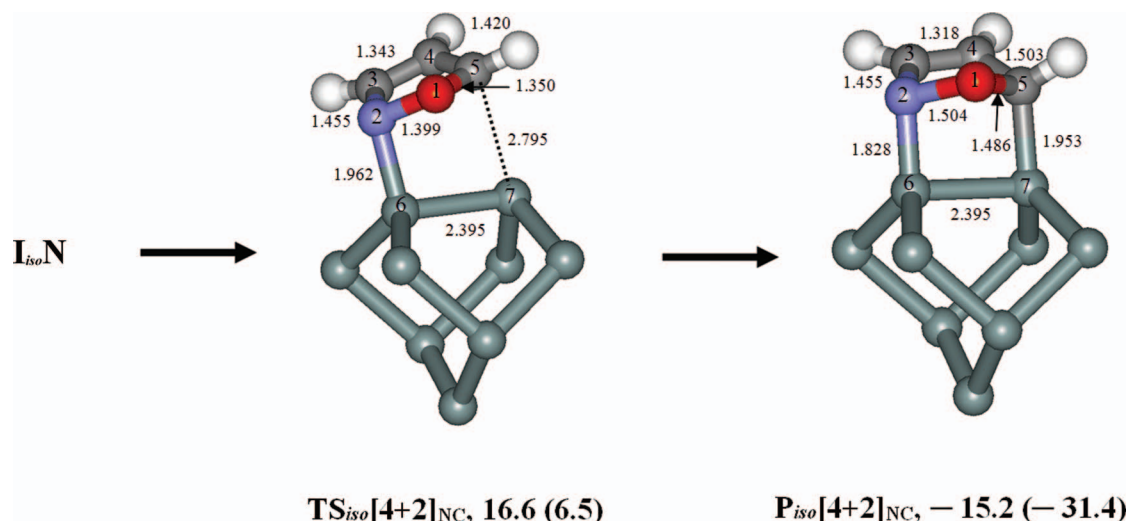


FIG. 6. The CASSCF transition states and intermediates along the [4+2] cycloaddition channel of isoxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

which is much higher than those of Si–O adduct(*I*<sub>iso</sub>O) and [2+2]<sub>NC</sub> product(*P*<sub>iso</sub>[2+2]<sub>NC</sub>) paths. Although the [2+2]<sub>CC</sub> product(*P*<sub>iso</sub>[2+2]<sub>CC</sub>) is more stable than of Si–O adduct(*I*<sub>iso</sub>O) and [2+2]<sub>NC</sub> product(*P*<sub>iso</sub>[2+2]<sub>NC</sub>), but its high reaction barrier makes it kinetically the least favorable. The two Si–C bond lengths in TS<sub>iso</sub>[2+2]<sub>CC</sub> are calculated to be 2.10 and 2.97 Å indicating an asymmetric transition state. The similar direct [2+2]<sub>CC</sub> path was also found in oxazole as shown in Figure 5. The transition state(TS<sub>oxa</sub>[2+2]<sub>CC</sub>) directly connects the reactants and the [2+2]<sub>CC</sub> product (*P*<sub>oxa</sub>[2+2]<sub>CC</sub>). The predicted reaction barrier is 20.9 kcal/mol, which is still much higher than the [2+2]<sub>NC</sub> barrier.

In short, although the [2+2]<sub>CC</sub> cycloadditions of isoxazole and oxazole form slightly more stable products, their large barriers make them kinetically less favorable.

### C. Direct and indirect [4+2] cycloaddition reaction channels

*Stepwise Mechanism of [4+2]<sub>NC</sub> Products:* The formation of the two side-on states follows the so-called [4+2] cycloaddition mechanism, as previously revealed for the chemisorption of benzene,<sup>10</sup> 1,3-cyclohexadiene,<sup>7–9</sup> and pyridine,<sup>12</sup> on the Si(100)-2 × 1 surface. 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] products. In the case of isoxazole and oxazole proceed the [4+2] cycloaddition through only 2 and 5 positions of the ring. Due to the geometric arrangement of nitrogen, the [4+2]<sub>NC</sub> cycloaddition of isoxazole involve one nitrogen atom as shown in Figure 6. Here the subscript NC was added to emphasize the Si–N bond. On the other hand, the oxazole undergoes directly without involving Si–N

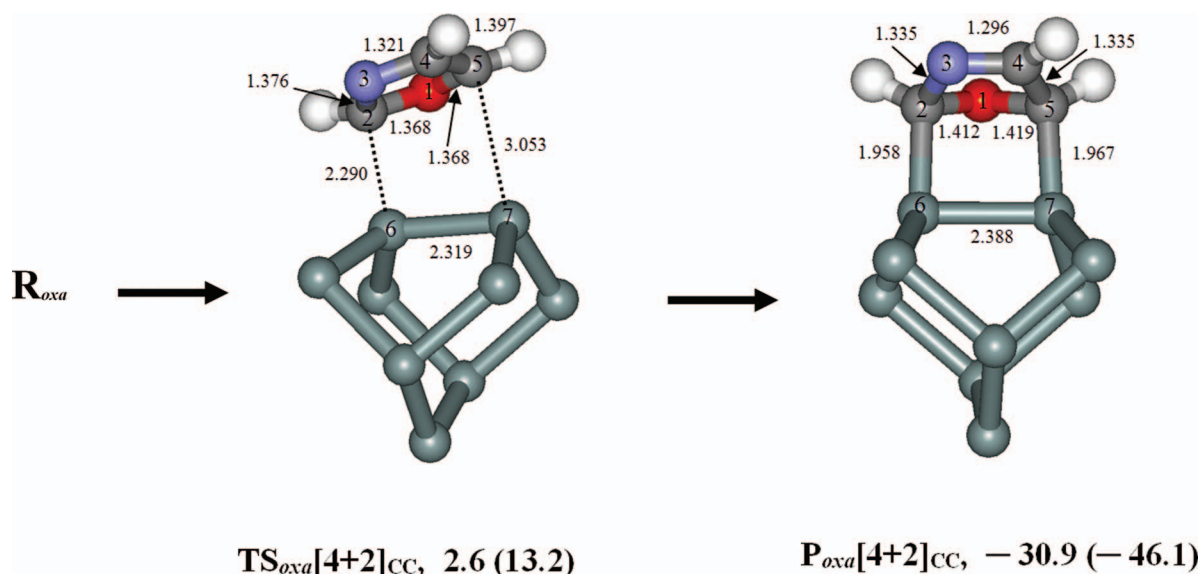


FIG. 7. The CASSCF transition states and intermediates along the [4+2] cycloaddition channel of oxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.



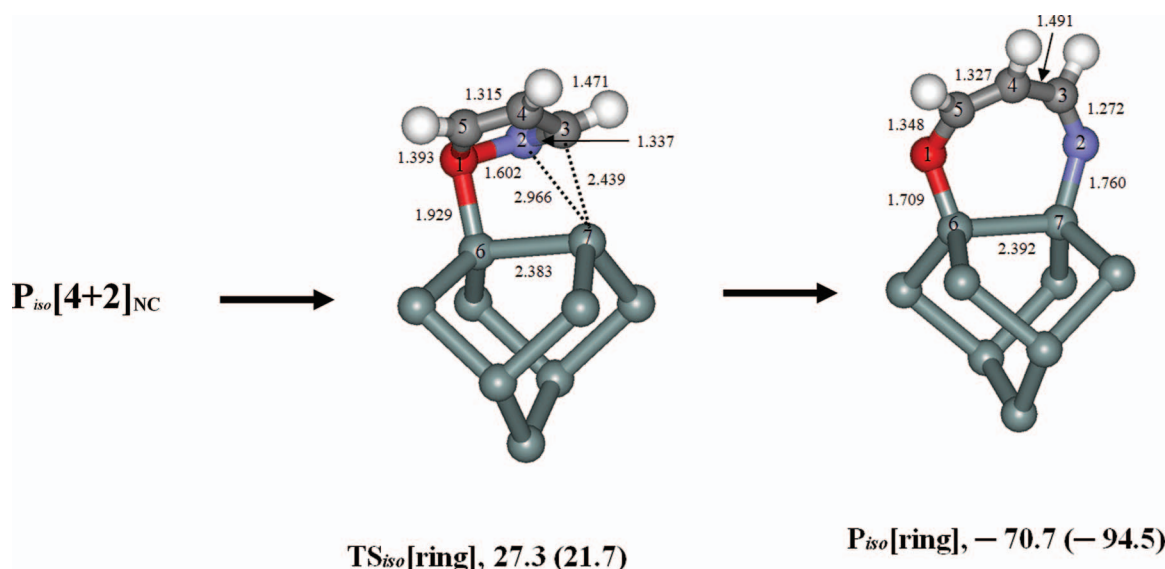


FIG. 8. The CASSCF transition states and intermediates along the N-O  $\sigma$  bond cleavage channel of isoxazole. Relative energies are obtained with SIMOMM:MRMP2/6-31G(d). The values in parentheses are obtained with SIMOMM:CASSCF/6-31G(d). Geometric data are from the CASSCF results.

bond. Consequently, the characteristics of the two [4+2] cycloadditions turned out to be distinctly different. The [4+2]<sub>NC</sub> product ( $P_{iso}[4+2]_{NC}$ ) of isoxazole forms heterogeneous di- $\sigma$  bonds onto the surface dimer through its 2 and 5 positions. Thermodynamically, the [4+2]<sub>NC</sub> product ( $P_{iso}[4+2]_{NC}$ ) is in between the most stable Si-N dative adduct and the [2+2]<sub>CC</sub>. Transition state  $TS_{iso}[4+2]_{NC}$  connects the Si-N adduct ( $I_{iso}N$ ) and the [4+2]<sub>NC</sub> product ( $P_{iso}[4+2]_{NC}$ ) with the reaction barrier of 16.6 kcal/mol. Although it is lower than [2+2]<sub>CC</sub> path, the value is unexpectedly large considering the symmetry allowed [4+2] mechanism. As a result, this [4+2]<sub>NC</sub> path is kinetically less accessible than the [2+2]<sub>NC</sub>. Therefore, the [4+2]<sub>NC</sub> product ( $P_{iso}[4+2]_{NC}$ ) is not particularly favorable. Structurally the  $TS_{iso}[4+2]_{NC}$  has a very asymmetric configuration, since the Si<sub>6</sub>-N<sub>2</sub> and Si<sub>7</sub>-C<sub>5</sub> bond distances are calculated to be 1.96 and 2.80 Å, which deviate from the ideal symmetry allowed [4+2] transition structure. Since the [4+2]<sub>NC</sub> requires Si-N dative bond adduct, its mechanism should be classified as a stepwise path.

**Concerted Mechanism of [4+2]<sub>CC</sub> Products:** In contrast, the corresponding [4+2] reaction of oxazole forms two Si-C bonds without involving nitrogen. The [4+2]<sub>CC</sub> reaction barrier of oxazole ( $TS_{oxa}[4+2]_{CC}$ ) is predicted to be 2.6 kcal/mol, which is negligibly small (see Figure 7). In addition, the stabilization energy of [4+2]<sub>CC</sub> product ( $P_{oxa}[4+2]_{CC}$ ) is predicted to be 30.9 kcal/mol, which is even more stable than the initial Si-N adduct, making the [4+2]<sub>CC</sub> path kinetically and thermodynamically the most favorable.

At this point, it is interesting to compare the chemisorption behavior of oxazole with furan<sup>28</sup> on the same surface. Furan preferentially undergoes the [4+2] cycloaddition reaction and formed di- $\sigma$  bonded 2,5-dihydrofuran-like adspecies. This process is barrierless and exothermic with the predicted energies of -30.0 kcal/mol at B3LYP/6-31G(d) level of theory, which agrees well with those of oxazole.

#### D. Side reaction channel

**Reaction Mechanism of N-O  $\sigma$ -Bond Cleavage in Isoxazole:** One interesting side reaction is the N-O bond cleavage yielding a very stable surface product in the case of isoxazole. The reaction starts from the [4+2]<sub>NC</sub> of isoxazole as in Figure 8. By breaking O<sub>1</sub>-N<sub>2</sub> and Si<sub>7</sub>-C<sub>3</sub> and making Si<sub>7</sub>-N<sub>2</sub> bond, the transition state  $TS_{iso}[\text{ring}]$  connects the [4+2]<sub>NC</sub> ( $P_{iso}[4+2]_{NC}$ ) and the very stable 7-membered ring ( $P_{iso}[\text{ring}]$ ) with the reaction barrier of 27.3 kcal/mol which is higher than the [2+2]<sub>NC</sub> and [4+2]<sub>NC</sub> channels by 15.0 and 10.7 kcal/mol, respectively, but lower than [2+2]<sub>CC</sub> cycloaddition channel by 9.3 kcal/mol. Although it has intermediate height of reaction barrier, the resulted ring opening product  $P_{iso}[\text{ring}]$  is the most stable product with the stabilization energy of 70.7 kcal/mol. The similar ring opening was not found for oxazole. Therefore, it is a unique product of isoxazole. The  $P_{iso}[\text{ring}]$  can be formed if enough thermal energy can be provided. Once it is formed, it would not be converted to other product.

#### IV. CONCLUSIONS

The surface reaction pathways of isoxazole and oxazole on Si(100)-2  $\times$  1 surface were theoretically investigated. The overall energetics is summarized in Schemes 1 and 3. These two molecules commonly attached with Si(100) surface through Si-N dative bond addition forming a stable initial adduct. In the case of isoxazole, Si-O dative bond adduct, [2+2]<sub>NC</sub> and [4+2]<sub>NC</sub> products can be formed from the initial Si-N dative bond adduct as a stepwise fashion. These three reactions have relatively sizable reaction barriers. The resulted products are not as stable as the initial Si-N adduct. The very large reaction barrier of the direct [2+2]<sub>CC</sub> cycloaddition of isoxazole makes it kinetically the least accessible.

Consequently, the initially formed Si–N adduct can be the major surface product in the adsorption of isoxazole.

In the case of oxazole, the similar stepwise  $[2+2]_{\text{NC}}$  and direct  $[2+2]_{\text{CC}}$  reaction were found. However, unlike isoxazole, a concerted  $[4+2]_{\text{CC}}$  cycloaddition without involving the initial Si–N dative bond adduct was found with very small reaction barrier (see Scheme 3). It is due to the particular arrangement of the two heteroatoms of oxazole as compared to isoxazole in such a way that the two Si–C  $\sigma$ -bonds can be formed. Therefore, not only Si–N dative bond adduct but also the  $[4+2]_{\text{CC}}$  can be expected in oxazole.

An interesting N–O bond cleavage reaction was found in the case of isoxazole. Although it has a large reaction barrier, the final outcome becomes very stable. Therefore, once N–O cleavage occurs, it would not be converted into other products.

Experiment<sup>13</sup> shows that adsorptions of both isoxazole and oxazole on Si(111) surface yield dative-bond addition, which is consistent with our results. In the case of cycloaddition, isoxazole and oxazole formed  $[4+2]$ -like and  $[2+2]$ -like cycloaddition on Si(111), respectively. Our study on Si(100) surface also shows  $[4+2]$  and  $[2+2]$  products both of isoxazole and oxazole. However, facile  $[4+2]$  reaction can only occur in the adsorption of oxazole, which does not appear in the corresponding experiment. This discrepancy between theory and experiment may be due to the different surface (Si(100) vs. Si(111)). More comparative study between these surfaces is expected.

In short, the geometric arrangements and electronegativity of heteroatoms of these molecules significantly affect the existing initial adsorption potential energy surfaces. The unique atom arrangements of these two molecules give rise to differences in competition and selectivity of reaction channels.

## ACKNOWLEDGMENTS

This work was supported by National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2011-0001213 and No. 2011-0005032).

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