

Addition Reaction of Nitrones on the Reconstructed Si(100)-2 × 1 Surface

Yongjun Liu^{*,†,‡} and Zhiguo Wang[†]

School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, China and Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining, Qinghai, 810001, China

Received: November 28, 2006; In Final Form: January 21, 2007

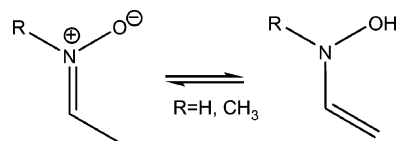
The reaction of nitron, *N*-methyl nitron, and their hydroxylamine tautomers (vinyl-hydroxylamine and *N*-methyl vinyl-hydroxylamine) on the reconstructed Si(100)-2 × 1 surface has been investigated by means of hybrid density functional theory (B3LYP) and Møller-Plesset second-order perturbation (MP2) methods. The calculations predicted that both of the nitrones should react with the surface dimer via facile concerted 1,3-dipolar cycloaddition leading to 5-member-ring compounds. The reaction of hydroxylamine tautomers on the Si(100) surface follows π -complex (intermediate) mechanism. For the reaction of *N*-methyl vinyl-hydroxylamine, the π -complex intermediate undergoes [2+2] cycloaddition leading to a 4-member-ring compound. But in the reaction of vinyl-hydroxylamine, the intermediate undergoes H-migration reaction (“ene” reaction) resulting in the oxime-terminated Si surface. All the surface reactions result in the hydroxyl-terminated silicon surfaces, which are very useful for the further modification of the semiconductor.

1. Introduction

The covalent attachment of organic molecules on silicon surfaces have attracted particular interest not only for industrial purposes but also for scientific interest.^{1–6} Since the seminal work reported by Chidsey and co-workers a decade ago, many methods for preparing a hybrid organic–silicon system have been developed involving wet chemical and ultrahigh-vacuum (UHV) approaches.^{7–13} Among these, a promising approach is the addition reaction of unsaturated organic compounds on the Si(100) surface because of its simplicity in operation, mild reaction conditions, and high selectivity. In the past decade, the cycloaddition reactions of simple and conjugated alkene/alkyne derivatives with the Si(100) surface have been extensively studied.^{14–22} Most theoretical investigations revealed that the [2+2] and [4+2] cycloadditions follow a stepwise mechanism by means of a π -complex precursor and a diradical intermediate.^{17a,18,22} However, the study of 1,3-dipolar cycloaddition of 1,3-dipoles on the Si(100) surface is still very limited. Barriocanal et al. studied the 1,3-dipolar cycloaddition of nitromethane on the Si(100) surface.²³ Lu and co-workers investigated the 1,3-dipolar cycloadditions of a series of small 1,3-dipolar molecules onto the C(100) surface.²⁴

In fact, the 1,3-dipolar cycloaddition reaction is probably the second most important cycloaddition reaction after the Diels–Alder reactions. In particular, the reaction of nitrones with simple alkenes has received great attention in asymmetric synthesis. One of the reasons is that contrary to the majority of other 1,3-dipoles, most nitrones are stable compounds that do not require in situ formation. On the other hand, in the 1,3-dipolar cycloaddition reaction of nitrones up to three new contiguous chiral centers can be formed and the adduct (isoxazolidine) can be transformed into numerous attractive building-block molecules.

SCHEME 1



On the native Si(100) surface, each surface silicon atom has a “dangling bond” with one electron in each. Therefore, on thermally reconstructed Si surface, the surface Si atoms can easily pair into dimers with partial characteristic of double bond. Because of the nonplanar geometry on the surface dimer, the π overlap in the surface dimer is poor and the silicon surface is very reactive. Both experimental and theoretical studies revealed that the surface dimer reacts with many kinds of unsaturated organic compounds to form numerous addition products.^{7–22} The typical addition reactions are cycloaddition reactions of [4+2] (Diels–Alder reaction) with conjugated dienes and [2+2] with simple alkenes.

To explore a new type of surface reaction that can be used to functionalize silicon surface, the present work makes an effort to investigate the addition reactions of nitrones on the reconstructed Si(100)-2 × 1 surface. Nitrones with α -hydrogen could isomerize to their hydroxylamine tautomers (see Scheme 1), which possess the reactive C=C double bond. Therefore, the reactions of hydroxylamine tautomers on the Si(100) surface were studied also.

2. Computational Method

All calculations were carried out by using the Gaussian 98 program package. The geometric parameters of the reactants, intermediates, and transition states were fully optimized at UB3LYP/6-31G(d) level and confirmed by vibrational analysis. On a potential energy surface, all optimized geometries correspond to a local minimum that has no imaginary frequency mode or to a saddle point that has only one imaginary frequency mode. For comparison, the single-point calculations using MP2

* Corresponding author. E-mail: yongjunliu_1@sdu.edu.cn. Fax: (+86) 531 885 644 64.

[†] Shandong University.

[‡] Chinese Academy of Sciences.

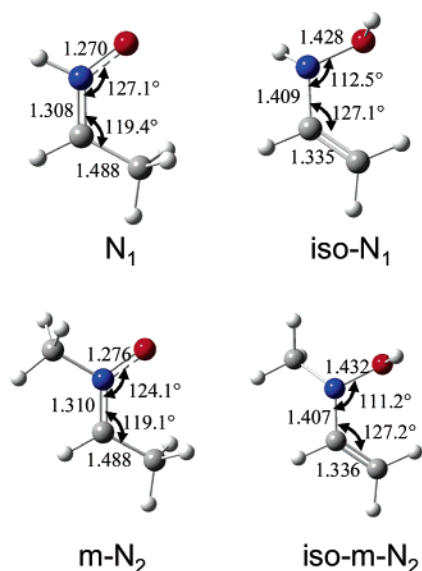


Figure 1. Structures of nitronium (N_1), N -methyl nitronium (m- N_2), and their hydroxylamine tautomers vinyl-hydroxylamine (iso- N_1) and N -methyl vinyl-hydroxylamine (iso-m- N_2) calculated at UB3LYP/6-31G(d) level. Lengths are in 0.1 nm and angles are in degrees.

with a basis set of 6-31G(d) were performed at the UB3LYP/6-31G(d) optimized structures.

We employed Si_9H_{12} cluster model to represent a dimer site on the Si(100)- 2×1 surface, which has been widely used in the theoretical investigation of addition reaction on silicon surface.^{15,18,22}

3. Results and Discussions

The most commonly used substituent at the nitrogen atom of nitronium is the phenylethyl group because it can be removed from the resulting adduct by hydrogenolysis.²⁵ For the sake of simplicity, we only studied nitronium and N -methyl nitronium.

Nitroniums with an α -hydrogen are in equilibrium with the hydroxylamine tautomer.²⁶ Our calculations indicated that nitronium and N -methyl nitronium could isomerize to their hydroxylamine tautomers with barriers of 146.5 and 144.5 kJ/mol, respectively.²⁷ The optimized structures of nitronium (N_1), N -methyl nitronium (m- N_2), and their hydroxylamine tautomers (denoted as iso- N_1 and iso-m- N_2 , respectively) are shown in Figure 1.

Nitronium (N_1) and N -methyl nitronium (m- N_2) are typical 1,3-dipoles, which could undergo 1,3-dipolar cycloaddition. Their hydroxylamine tautomers possess C=C double bonds that can be described as ethylene derivatives, which could also react with the Si(100) surface. Therefore, in this study two kinds of reactions were considered: (1) 1,3-dipolar cycloaddition of nitronium and N -methyl nitronium and (2) addition reaction of the hydroxylamine tautomers with surface dimer, as shown in Figure 2.

3.1. 1,3-Dipolar Cycloaddition of Nitroniums. We have investigated the reaction mechanism of 1,3-dipolar cycloaddition for nitronium (N_1) and N -methyl nitronium (m- N_2) on the Si(100) surface. To establish the initial geometries, the nitroniums were positioned above the Si=Si dimer with the distance of Si-O and Si-C being 3.00 Å. Because of the second-order Peierls distortion,²⁸ the lowest energy Si(100) dimer structure is asymmetric (i.e., one dimer atom is more electron rich than the other) giving the Si=Si bond a dipolar character. Therefore, in our calculation the electron-rich oxygen atom of nitronium was oriented to the electron-poor Si atom. We found no evidence

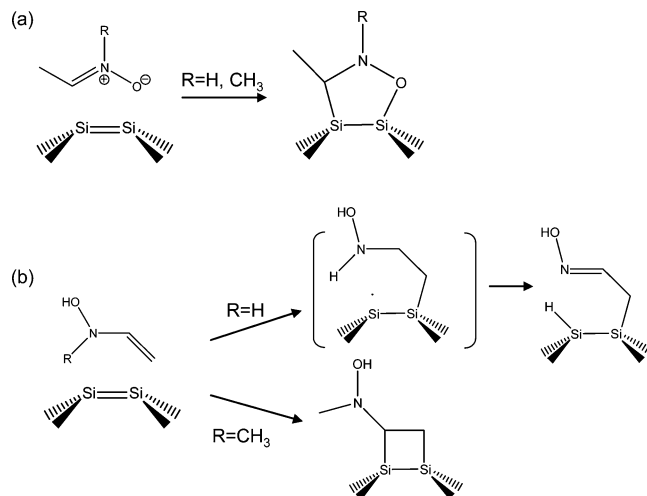


Figure 2. Possible reaction pathways. (a) 1,3-dipolar cycloaddition of nitronium and N -methyl nitronium; (b) addition reaction of hydroxylamine tautomers.

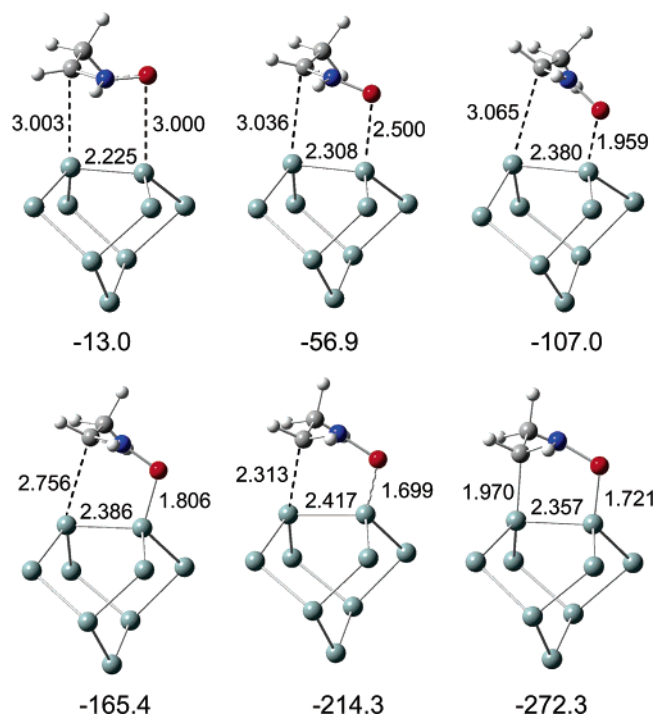


Figure 3. A series of geometries on the reaction path for 1,3-dipolar addition of nitronium obtained by stepwise optimization with ZPE-uncorrected energies calculated at the UB3LYP/6-31G(d) level in kJ/mol relative to the isolated reactants. Lengths are in 0.1 nm.

for an activation barrier between the separated reactants and the 1,3-dipolar cycloaddition adducts. Instead, the products were reached on asymmetric reaction paths by simply minimizing the energies from the initial geometries. It is similar to the 1,3-dipolar cycloaddition of nitromethane on the Si(100) surface.²³ The series of geometries and relative energies on the reaction paths for nitronium (N_1) and N -methyl nitronium (m- N_2) are shown in Figure 3 and 4, respectively.

Figure 3 shows that the relative positions of nitronium to the surface dimer changes with the forming of the first Si-O bond. After the distance of Si-O reached ~ 1.8 Å, the distance of Si-C decreased to ~ 2.8 Å. With the formation of the second Si-C bond, a large amount of association energy was released.

N -methyl nitronium is similar to nitronium so the influence of substituent on the 1,3-dipolar cycloaddition is not obvious.

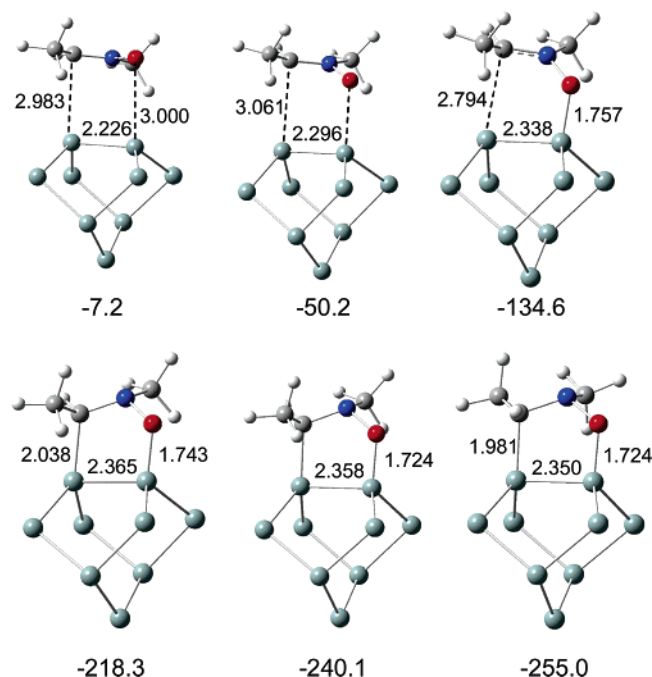


Figure 4. A series of geometries on the reaction path for 1,3-dipolar addition of *N*-methyl nitron obtained by stepwise optimization with ZPE-uncorrected energies calculated at the UB3LYP/6-31G(d) level in kJ/mol relative to the isolated reactants. Lengths are in 0.1 nm.

Experimental evidence has indicated that most 1,3-dipolar additions to C=C bonds follow a concerted path, and the first-principles calculations are in agreement with this picture.^{29–31} However, recent studies of 1,3-dipolar cycloadditions on the C(100)-2 × 1 surface indicated that the reaction undergoes stepwise mechanism,²⁴ which is different from our calculations on the Si(100)-2 × 1 surface. There are several reasons for the difference. First, the Si dimer π -bond is weaker than that of C dimer, so there is little energy cost to overcome before the surface can form a bond to the incoming molecules. Second, the initial stage of the 1,3-dipolar addition of nitrones on the Si(100) surface involves the formation of an Si–O bond. Because the Si–O bond energies (108 kcal/mol) are much stronger than those of the C–O bond (86 kcal/mol),³² the formation of the Si–O bond lowers the barrier more effectively than in the reaction with C(100) surface.

3.2. Addition Reaction of Hydroxylamine Tautomers.

UB3LYP calculations predicted that the reactions of ethylene derivatives with the Si(100) surface follow a stepwise mechanism:^{18,22} first, the C=C double bond of ethylene derivatives reacts with a surface Si atom to form a weakly bonded π -complex intermediate; second, the intermediate transformed to a singlet diradical intermediate via a transition state with the forming of the first Si–C bond; finally, the singlet diradical intermediate undergoes a ring-closing reaction to form the [2+2] cycloaddition product. Recently, Gordon and co-workers used multireference wave functions to study the surface reaction of 2-butene.^{17b} They found that 2-butene surface reaction follows a different reaction channel, the well-known “ene” reaction in organic chemistry, in which a methyl hydrogen transfers to the Si(100) surface.

Our calculations predicted that the reaction of hydroxylamine tautomers of nitrones on the Si(100) surface followed a similar but different mechanism (see Figure 2). Vinyl-hydroxylamine (iso-*N*₁) undergoes an H-migration reaction (ene reaction) leading to an oxime-terminated Si surface while that of *N*-methyl

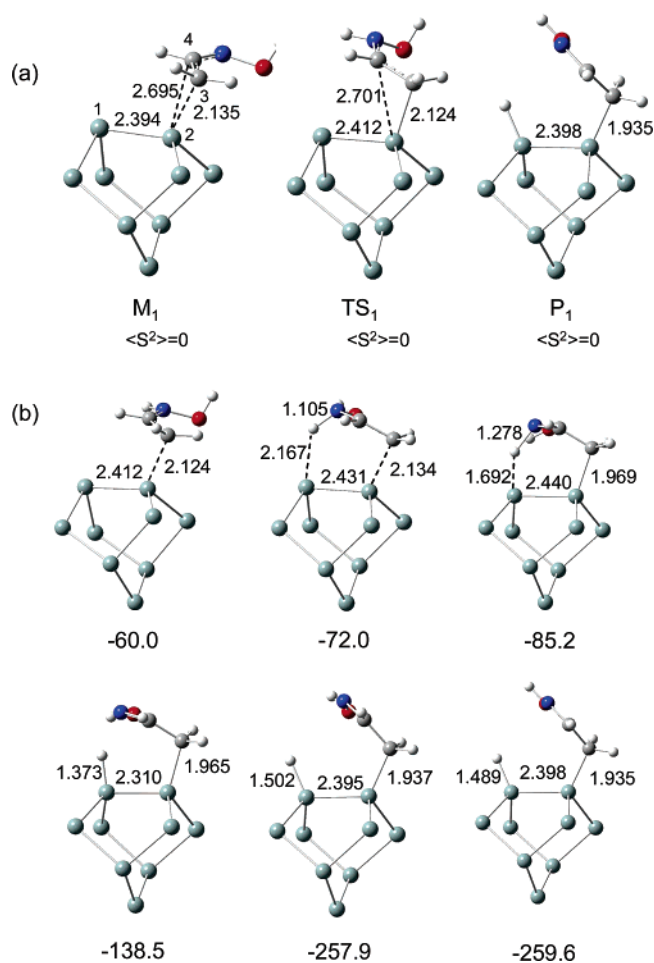


Figure 5. (a) Optimized geometric structures for intermediate (M_1), transition state (TS_1), and product (P_1). The values of $\langle S^2 \rangle$ for the wave functions of these stationary points are also given. (b) A series of geometries on the reaction path from transition state (TS_1) to product (P_1) obtained by stepwise optimization with ZPE-uncorrected energies calculated at the UB3LYP/6-31G(d) level in kJ/mol relative to the isolated reactants. Lengths are in 0.1 nm.

vinyl-hydroxylamine (iso-*m*-*N*₂) follows the [2+2] cycloaddition reaction resulting in a 4-member-ring product.

3.2.1. Ene Reaction of Vinyl-hydroxylamine (iso-*N*₁). Studies have shown that in addition to the [2+2] cycloaddition, some ethylene derivative with α -hydrogen such as propylene and 2-butene can undergo another potential competing reaction, the ene reaction.^{15a,17b} Vinyl-hydroxylamine (iso-*N*₁) possesses α -hydrogen on the nitrogen atom. Therefore, the surface reaction of vinyl-hydroxylamine on the Si(100) surface is expected to undergo the ene reaction. Our calculation indicated that vinyl-hydroxylamine could undergo a facile ene reaction with a negligible activation barrier. The geometrical feature of intermediate (M_1), transition state (TS_1), and product (P_1) are shown in Figure 5a.

Figure 5a shows that vinyl-hydroxylamine (iso-*N*₁) first forms a three-centered π -complex intermediate (M_1) between the two carbon atoms of the C=C bond and one Si atom of the Si=Si bond, which is very similar to the reaction of the ethylene derivative with the Si(100) surface.^{18,22} In the π -complex intermediate formed by the ethylene and Si(100)-2 × 1 surface, the Si=Si bond length is 2.363 Å and the distance Si–C is 2.406 Å.^{18b} But in the structure of M_1 , the bond length of Si=Si bond is 2.394 Å and the distances of the two Si–C bonds are 2.135 and 2.695 Å, respectively, suggesting a stronger interaction between the C=C double bond and surface Si atom

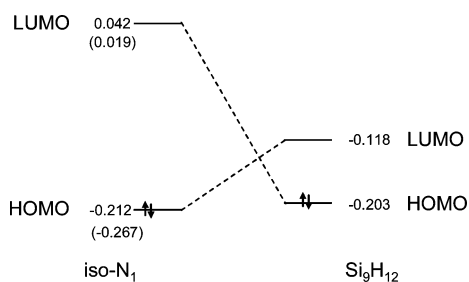


Figure 6. UB3LYP/6-31G(d) calculated energies of HOMO and LUMO of vinyl-hydroxylamine (iso-N₁) and Si₉H₁₂ in atomic unit. Values in parenthesis are the HOMO and LUMO of ethylene.

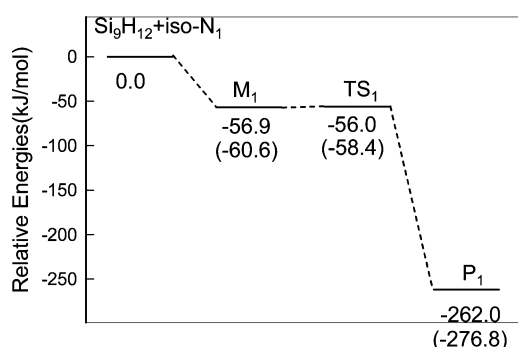


Figure 7. Energy profile for the addition reaction of vinyl-hydroxylamine (iso-m-N₁) nitrene with Si₉H₁₂ at UB3LYP/6-31G(d) level. Values in parentheses are calculated at UMP2/6-31G(d) level at the UB3LYP/6-31G(d) optimized geometries. All the energies are ZPE-corrected values.

than that of ethylene. This can be understood by examining the frontal orbitals of vinyl-hydroxylamine (iso-N₁), ethylene, and Si₉H₁₂ cluster.

The HOMO and LUMO energies of the vinyl-hydroxylamine (iso-N₁), ethylene, and Si₉H₁₂ are shown in Figure 6. Because of the smaller energy gap between HOMO of vinyl-hydroxylamine (iso-N₁) and LUMO of Si₉H₁₂ than that between the HOMO of the Si₉H₁₂ and the LUMO of vinyl-hydroxylamine, vinyl-hydroxylamine plays the role of π -electron donors whereas the Si=Si bond is the acceptor. The π -electron-donating abilities usually increase with the HOMO energy of the donor. Figure 6 shows that the HOMO of the vinyl-hydroxylamine is much higher than that of ethylene. Therefore, there is stronger interaction between the C=C double bond and Si(100) surface than that of ethylene.

The energy profile on the ene reaction path is shown in Figure 7. From Figure 7, one can see that M₁ undergoes a transition state (TS₁) leading to the oxime-terminated Si surface (P₁) with a negligible activation barrier. In TS₁, the distance of Si(2)–C(1) decreased to 2.124 from 2.135 Å, and the dihedral of Si(1)Si(2)C(3)C(4) changed from –60.2 to –36.5°. Because of the larger distance of Si(1)–C(4) (3.439 Å), Si(1)–N (4.200 Å), and Si(1)–O(5.100 Å) in TS₁, the energy profile is smooth when the geometries changed from M₁ to TS₁.

A series of the geometries and relative energies on the reaction path from TS₁ to the product (P₁) are shown in Figure 5(b). As shown in Figure 5(b), at the first stages when the moiety of vinyl-hydroxylamine molecule rotates along Si(1)–C(3), the total energies only decrease a little and the distances of Si(1)–Si(2) and Si(2)–C(3) remain almost unchanged. But with the approach of the H atom on the nitrogen to the Si(1) atom, the energy starts to drop sharply. After the hydrogen migrates to the silicon surface, the hydroxylamine functional group transforms to a oxime group.

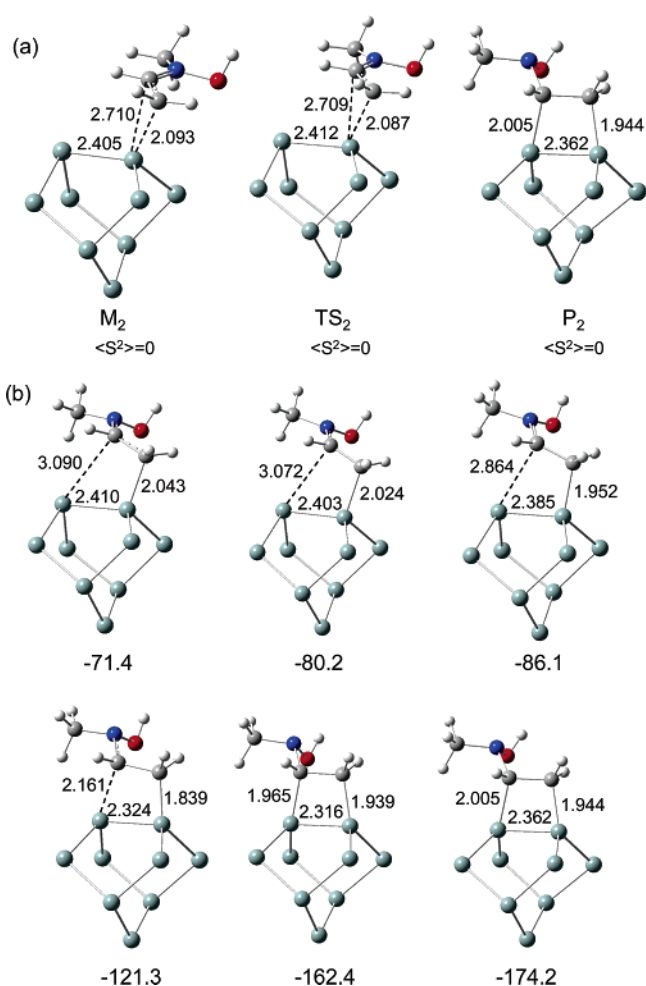


Figure 8. (a) Optimized geometric structures for intermediate (M₂), transition state (TS₂), and product (P₂). The values of $\langle S^2 \rangle$ for the wave functions of these stationary points are also given. (b) A series of geometries on the reaction path from transition state (TS₂) to product (P₂) obtained by stepwise optimization with ZPE-uncorrected energies calculated at the UB3LYP/6-31G(d) level in kJ/mol relative to the isolated reactants. Lengths are in 0.1 nm.

3.2.2. [2+2] Cycloaddition of *N*-Methyl vinyl-hydroxylamine (iso-m-N₂). Our calculations predicted that the addition reaction of *N*-methyl vinyl-hydroxylamine (iso-m-N₂) with the Si(100) surface follows [2+2] cycloaddition mechanism. Like the reaction of vinyl-hydroxylamine on the Si(100) surface, the reaction of *N*-methyl vinyl-hydroxylamine is also initiated by the formation of a π -complex intermediate (M₂), releasing a large amount of energy (71.3 kJ/mol). The intermediate (M₂) then transferred to the cycloaddition product (P₂) via a very small barrier transition state (TS₂). The geometrical feature of M₂, transition state (TS₂), and product (P₂) are shown in Figure 8a. The energy profile of the reaction path is drawn in Figure 9.

As shown in Figure 8(a) and 9, the three-centered π -complex intermediate (M₂) has the similar Si(2)–C(3) bond length as that of vinyl-hydroxylamine, implying a weak influence of substituent (methyl group on nitrogen) on the interaction between the C=C double bond and the Si atom of the Si=Si dimer. This is in accord with the similar HOMO and LUMO energies of vinyl-hydroxylamine and *N*-methyl vinyl-hydroxylamine.³³

The intermediate (M₂) transfers directly to the [2+2] cycloaddition product (P₂) via a very small barrier transition state (TS₂), which is unlike the addition of the ethylene derivative

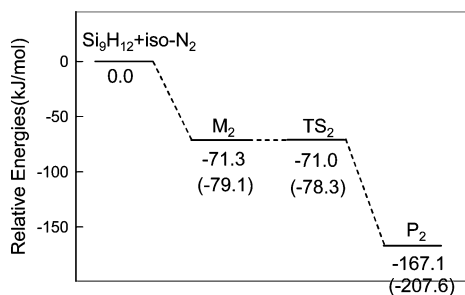


Figure 9. Energy profile for the addition reaction of *N*-methyl vinylhydroxylamine (iso-*m*-N₂) with Si₉H₁₂ at UB3LYP/6-31G(d) level. Values in parentheses are calculated at UMP2/6-31G(d) level at the UB3LYP/6-31G(d) optimized geometries. All the energies are ZPE-corrected values.

with Si(100) that undergo a diradical intermediate. A series of the geometries and relative energies on the reaction path from TS₂ to the product (P₂) are shown in Figure 8(b). Calculations indicated that at the first stages the moiety of *N*-methyl vinylhydroxylamine molecule rotates along Si(1)–C(3) and the total energies decrease smoothly with the decrease of the distance of Si(1)–C(4). After the bond length of Si(1)–C(4) reached ~2.0 Å, the total energy decreased sharply and the [2+2] cycloaddition product (P₂) was formed.

4. Conclusions

The surface reaction of nitron, *N*-methyl nitron, and their hydroxylamine tautomers on the reconstructed Si(100)-2 × 1 surface has been investigated by means hybrid density functional theory (B3LYP) and Møller-Plesset second-order perturbation (MP2) methods. The calculations predicted that the nitrones should react with the surface dimer via facile concerted 1,3-dipolar cycloaddition leading to 5-member-ring compounds. The reaction of hydroxylamine tautomers on the Si(100) surface follows π-complex mechanism. The two carbon atoms of the C=C bond first form π-complex (intermediate) with one Si atom of the surface dimer. Then the intermediates transform to the final products via transition states with negligible barriers. For the tautomer of *N*-methyl nitron, the intermediate undergoes [2+2] cycloaddition leading to a 4-member-ring compound. But in the reaction of the nitron, the intermediate undergoes H-migration reaction resulting in oxime-terminated Si surface. Because of the larger barrier of the isomerization of nitron, the favored reaction of nitron on the Si(100) surface is 1, 3-dipolar cycloaddition.

Acknowledgment. This work was supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars (State Education Ministry) and the Program of Hundreds Talent of the Chinese Academy of Science. Partial calculations were carried out at the High-Performance Computational Center of Shandong University. The authors also thank Professor Yi Hu for his help in calculations.

Supporting Information Available: Detailed description of the isomerization of nitron and *N*-methyl nitron to their hydroxylamine tautomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Rakshit, T.; Liang, G.-C.; Ghosh, A. W.; Datta, S. *Nano Lett.* **2004**, *4*, 1803.
- (2) Sieval, A. B.; Linke, R.; Zuihof, H.; Sudhölter, E. J. R. *Adv. Mater.* **2000**, *12*, 1457.

- (3) (a) Wayner, D. D. M.; Wolkow, R. A. *J. Chem. Soc., Perkin Trans. 2*, **2002**, 23. (b) Lopinsky, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **2000**, *406*, 48.
- (4) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271.
- (5) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Jovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russel, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617.
- (6) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.
- (7) (a) Linford, M. R.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1993**, *115*, 12631. (b) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145. (c) Wagner, P.; Nock, S.; Spudich, J. A.; Volkuth, W. D.; Chu, S.; Cicero, R. L.; Wade, C. P.; Linford, M. R.; Chidsey, C. E. D. *J. Struct. Biol.* **1997**, *119*, 189. (d) Cicero, R. L.; Lindord, M. R.; Chidsey, C. E. D. *Langmuir* **2000**, *16*, 5688. (e) Cicero, R. L.; Chidsey, C. E. D.; Lopinsky, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Langmuir* **2002**, *18*, 305.
- (8) (a) Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; van der Maas, J. H.; de Jeu, W. H.; Zuihof, H.; Sudhölter, E. J. R. *Langmuir* **1998**, *14*, 1759. (b) Sieval, A. B.; Vleeming, V.; Zuihof, H.; Sudhölter, E. J. R. *Langmuir* **1999**, *15*, 8288. (c) Sieval, A. B.; Linke, R.; Heij, G.; Meijer, G.; Zuihof, H.; Sudhölter, E. J. R. *Langmuir* **2001**, *17*, 7554.
- (9) (a) Boukherroub, R.; Morin, S.; Bensebaa, F.; Wayner, D. D. M. *Langmuir* **1999**, *15*, 3831. (d) Boukherroub, R.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1999**, *121*, 11513.
- (10) (a) de Villeneuve, C. H.; Pinson, J.; Bernard, M. C.; Allongue, P. *J. Phys. Chem. B* **1997**, *101*, 2415. (b) Allongue, P.; de Villeneuve, C. H.; Pinson, J.; Ozanam, F.; Chazalviel, J. N.; Wallart, X. *Electrochim. Acta* **1998**, *43*, 2791.
- (11) (a) Fidelis, A.; Ozanam, F.; Chazalviel, J.-N. *Surf. Sci.* **2000**, *444*, L7. (b) Teyssot, A.; Fidelis, A.; Fellah, S.; Ozanam, F.; Chazalviel, J. -N. *Electrochim. Acta* **2002**, *47*, 2565.
- (12) (a) Bansal, A.; Li, X.; Lauermaun, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. H.; *J. Am. Chem. Soc.* **1996**, *118*, 7225. (b) Bansal, A.; Lewis, N. S. *J. Phys. Chem. B* **1998**, *102*, 1067. (c) Haber, J. A.; Lauermaun, I.; Michalak, D.; Vaid, T. P.; Lewis, N. S. *J. Phys. Chem. B* **2000**, *104*, 9947.
- (13) (a) Liu, Y.-J.; Navasero, N. M.; Yu, H.-Z. *Langmuir* **2004**, *20*, 4039. (b) Asanuma, H.; Lopinski, G. P.; Yu, H.-Z. *Langmuir* **2005**, *21*, 5013.
- (14) Hovis, J. S.; Liu, H.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 6873.
- (15) (a) Konečný, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169. (b) Konečný, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098. (c) Barriocanal, J. A.; Doren, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 7340.
- (16) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 4082.
- (17) (a) Chio, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **2002**, *124*, 6162. (b) Lee, H. S.; Chio, C. H.; Gordon, M. S. *J. Phys. Chem. B* **2005**, *109*, 5067. (c) Jung, Y.; Gordon, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 3131.
- (18) (a) Lu, X.; Zhu, M.; Wang, X. *J. Phys. Chem. B* **2004**, *108*, 7359. (b) Lu, X. *J. Am. Chem. Soc.* **2003**, *125*, 6384. (c) Lu, X.; Zhu, M.; Wang, X.; Zhang, Q. *J. Phys. Chem. B* **2004**, *108*, 4478.
- (19) Teague, L. C.; Chen, D. J.; Boland, J. J. *J. Phys. Chem. B* **2004**, *108*, 7827.
- (20) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 3548.
- (21) Minary, P.; Tuckerman, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 1110.
- (22) (a) Wang, Y.; Ma, J.; Inagaki, S.; Pei, Y. *J. Phys. Chem. B* **2005**, *109*, 5199. (b) Wang, Y.; Ma, J. *J. Phys. Chem. B* **2006**, *110*, 5542.
- (23) Barriocanal, J. A.; Doren, D. J. *J. Phys. Chem. B* **2000**, *104*, 12269.
- (24) (a) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Org. Chem.* **2002**, *67*, 515. (b) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, *106*, 5972.
- (25) Gothelf, K. V.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 863.
- (26) Arnó, M.; Zaragoza, R. J.; Domingo, L. R. *Tetrahedron: Asymmetry* **2004**, *15*, 1541.
- (27) For a detailed description of the potential energy surface profiles, see Supporting Information.
- (28) Burdett, J. K. *Chemical Bonding in Solids*; Oxford University Press: New York, **1995**.
- (29) Liu, J.; Niwayama, S.; You, Y.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 1064.
- (30) Su, M.-D.; Liao, H.-Y.; Chuang, W.-S.; Chu, S.-Y. *J. Org. Chem.* **1999**, *64*, 6710.
- (31) Nguyen, M. T.; Chandra, A. K.; Sakai, S.; Morokuma, K. *J. Org. Chem.* **1999**, *64*, 65.
- (32) Emsley, J. *The Elements*; Clarendon Press: Oxford, UK, **1993**.
- (33) The UB3LYP/6-31.G(d) calculated energies of HOMO and LUMO of *N*-methyl vinyl hydroxylamine are -0.204 and 0.041, respectively.