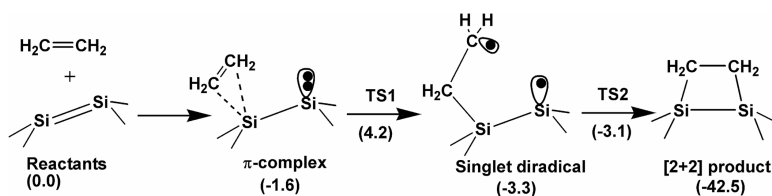


Diradical Mechanism for the [2 + 2] Cycloaddition of Ethylene on Si(100) Surface

Xin Lu

J. Am. Chem. Soc., **2003**, 125 (21), 6384-6385 • DOI: 10.1021/ja034779z • Publication Date (Web): 03 May 2003

Downloaded from <http://pubs.acs.org> on March 28, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 5 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Diradical Mechanism for the [2 + 2] Cycloaddition of Ethylene on Si(100) Surface

Xin Lu*

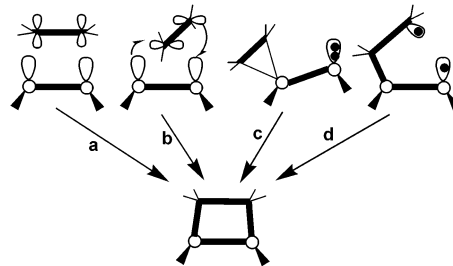
State Key Laboratory for Physical Chemistry of Solid Surface and Center for Theoretical Chemistry,
Department of Chemistry, Xiamen University, Xiamen 361005, China

Received February 20, 2003; E-mail: xinlu@xmu.edu.cn

Chemical modification of semiconductor silicon surfaces by using organic molecules with various functionalities has received much attention in the recent years as a result of the importance of semiconductors in microelectronics technology. The availability of a large number of organic molecules to form strong, uniform, and controlled organic silicon interfaces has been exploited.¹ Of particular interest is the attachment of alkenes on Si(100) surface, which has been shown to lead to a controllable organic monolayer on the surface with quite strong organic silicon binding.^{1–9} Rather interesting cycloaddition chemistry has been disclosed experimentally between simple alkenes and the Si=Si dimers of the reconstructed Si(100)-2 × 1 surface. That is, quite facile [2 + 2] cycloaddition, which seemingly “conflicts” with the Woodward–Hoffmann rules, occurs between the C=C bond of an alkene and a Si=Si dimer of Si(100) surface. Several possible reaction mechanisms (see Scheme 1) have been proposed to account for such a “symmetry-forbidden” pericyclic reaction.^{6–10} Controversy exists in the literature regarding the mechanism of such “symmetry-forbidden” pericyclic gas–surface reaction.^{8,9} In this communication, we show the reaction follows a diradical pathway, via a π -complex precursor and a diradical intermediate.

Among the four possible pathways given in Scheme 1, the direct, concerted pathway **a** and the antarafacial + superfacial pathway **b** are either symmetry-forbidden or sterically hindered and thus can be safely excluded.⁸ As the Si–Si dimer is buckled at low temperature,^{11,12} it is possible to have a low-symmetry pathway **c**, in which the incoming alkene forms a π -complex intermediate with the Si–Si dimer, followed by the formation of the [2 + 2] product.⁸ The last one, pathway **d**, is a diradical mechanism, i.e., a diradical intermediate is first formed and followed by ring-closing.⁹ Pathway **c** was believed to be stereospecific, i.e., the stereochemistry of the reactant alkene is retained in the reaction,⁸ whereas pathway **d** that allows rotation of the radical-end group in the diradical intermediate should be less stereospecific. On the basis of their IR experiments on the adsorption of *cis*- and *trans*-1,2-dideuterioethylene on Si(100), Liu et al. believed that the interaction of ethylene with Si(100) is stereospecific and would follow the low-symmetry pathway **c**.⁸ In contrast, the recent scanning tunneling microscopy (STM) experiments revealed that for the adsorption of *trans*-2-butene on Si(100), the [2 + 2] reaction is not stereospecific with a stereoselectivity of 98% and a small degree of isomerization, implying a diradical mechanism for the gas–surface reaction.⁹ Ab initio calculations of the pathway for the adsorption of simple alkenes on Si(100) surface are not available, even though a lot of theoretical studies have been reported regarding the conformation and distribution of the adsorbed alkenes on the surface.^{13–18} Two relevant papers have been reported concerning the mechanism for the adsorption of 1,3-cyclohexadiene, thiophene, and furan on Si(100).^{19,20} In addition to the barrierless [4 + 2] cycloaddition pathway, a kinetically less favorable [2 + 2] cycloaddition pathway

Scheme 1. Possible Pathways for the [2 + 2] Cycloaddition of a Simple Alkene with a Si=Si Dimer of Si(100) Surface



with a mono- σ bonded transition state, but no diradical intermediate, was predicted for these conjugated dienes on Si(100).^{19,20} It remains unclear whether the adsorption of an alkene on Si(100) would adopt a similar reaction mechanism and whether there is a diradical intermediate in the reaction pathway. Accordingly, we performed density functional cluster model calculations to explore the reaction pathway for ethylene adsorption on the Si=Si dimer of Si(100) surface.

All calculations were performed with Gaussian98.²¹ A Si₉H₁₂ cluster model was used to represent the Si=Si dimer of Si(100) surface.^{10,14,19,22} Geometries were fully optimized at the (U)B3LYP/6-31G* level.²³ Reported energies are zero-point energy (ZPE)-corrected. The predicted intermediates, transition states, and product are depicted in Figure 1.

The adsorption of ethylene is initiated by the formation of a weakly bonded π -complex **LM1**, which is 1.6 kcal/mol lower than the isolated reactants in energy. In **LM1**, a weak dative bond is formed between the π -bond of ethylene and the electron-deficient buckled-down Si atom;^{11,12} the shortest Si–C distance is 2.401 Å. By overcoming a barrier height of 5.8 kcal/mol at transition state **TS1**, a singlet diradical intermediate **LM2** is formed. **LM2** is 3.3 kcal/mol lower in energy than the isolated reactants. In **LM2**, the ethylene moiety is mono- σ bonded onto a Si atom with a Si–C bond length of 1.951 Å. The –CH₂ radical end group in the ethylene moiety is far away from the unreacted Si atom of the Si–Si dimer with a C–Si distance of 3.945 Å. From **LM2** ring-closing to form the final product, **LM3** is slightly activated with a small barrier of 0.2 kcal/mol at transition state **TS2**.

It is clear from our (U)B3LYP/6-31G* calculations that the rate-determining step for the [2 + 2] cycloaddition reaction between ethylene and the Si=Si dimer of Si(100) surface is the formation of the singlet diradical intermediate **LM2** but not the ring-closing step. The activation energy for the overall reaction predicted at the (U)B3LYP/6-31G* level is 4.2 kcal/mol, in line with the experimental estimation of 2.9 kcal/mol.⁴ Since it involves both a π -complex intermediate and a diradical intermediate, the reaction pathway shown in Figure 1 can be better regarded as a combination of the previously proposed pathways **c** and **d**. With a small binding energy (1.6 kcal/mol), the π -complex precursor of ethylene would

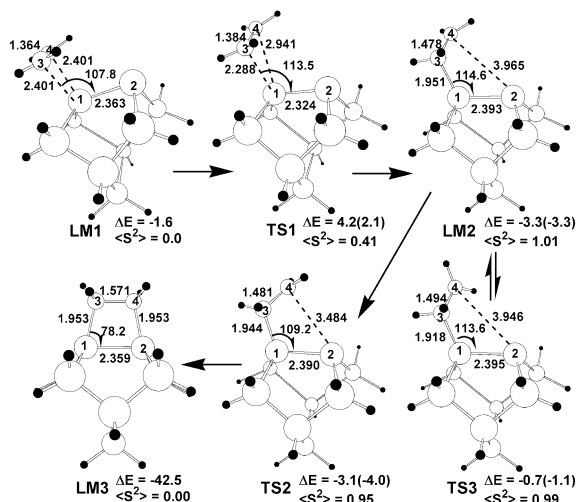


Figure 1. (U)B3LYP/6-31G* optimized intermediates (LM1 and LM2), transition states (TS1, TS2, and TS3) and product (LM3) for the [2 + 2] cycloaddition of ethylene on Si₉H₁₂ cluster model. Energies (ΔE in kcal/mol) relative to isolated ethylene and Si₉H₁₂ and the ⟨S²⟩ values for the wave functions of these stationary points are also given. Spin-projected energies are given in parentheses.

display high mobility, accounting for the coverage-dependence of sticking probability observed experimentally.⁴

Furthermore, a transition state TS3 which accounts for the intramolecular rotation of the -CH₂ radical group around the C-C bond in the diradical intermediate LM2 has been located. TS3 is 2.6 kcal/mol higher than LM2 and 0.7 kcal/mol lower than the isolated reactants in energy, indicating that the intramolecular isomerization is plausible at LM2. Accordingly, the stereochemistry of the reactant alkene can be altered in the [2 + 2] cycloaddition on the Si=Si dimer of Si(100), i.e., the reaction would not be stereospecific. However, ring-closing from LM2 to LM3 requires much lower activation energy than does the intramolecular isomerization at LM2, meaning that the probability for the reactant to undergo intramolecular isomerization at the diradical intermediate would be low. Hence, the gas-surface reaction should still display a high stereoselectivity. This is in full agreement with the previous STM observation.⁹

In summary, we predict, by means of density functional cluster model calculations, that the adsorption of ethylene on Si(100) surface follows a diradical mechanism, proceeding via a π-complex precursor and a singlet diradical intermediate. Our calculations confirmed the recent STM observation⁹ that the adsorption of an alkene on Si(100) is not stereospecific, but highly stereoselective, in nature. It is the rather weak π-bonding (bond strength of 5–10 kcal/mol)^{24a} in the surface Si=Si dimer that facilitates the formation of singlet diradical intermediate in such a heterogeneous [2 + 2] cycloaddition reaction. Note that the diamond (100) and germanium (100) surfaces, which display similar 2 × 1 reconstruction to Si(100) surface, consist of X=X dimers (X = C, Ge) with weak π-bond strengths (~28 kcal/mol for C(100)^{24b} and ~5 kcal/mol for Ge(100)^{24c}). We believe the adsorption of alkenes on these surfaces would follow similar diradical mechanisms. Such diradical mechanism accounts well for the experimental observation that the order of reactive sticking probabilities of alkenes on these surfaces, i.e., C(100) ≪ Ge(100) < Si(100), correlates negatively with the order of the π-π* surface-state band gaps of 315 kJ/mol for C(100), 140 kJ/mol for Ge(100), and ~110 kJ/mol for Si(100).^{1c,25} Furthermore, the presence of the radical intermediate also implies the probability for the formation of interdimer adspecies in the adsorption of alkenes and alkynes on these surfaces.^{21b,26} Theoretical

exploration of the diradical mechanism for the adsorption of ethylene on C(100) and Ge(100) surfaces is under way in our laboratory.

Acknowledgment. This work was sponsored by Fok Ying-Tung Educational Foundation, Nature Science Foundation of China (20203013, 20021002 and 20023001), the Ministry of Education of PRC (20010384005), the Ministry of Science and Technology (2002CCA01600), Natural Science Foundation of Fujian Province (E0210001 and 2002F010), and Xiamen University.

References

- (1) (a) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413. (b) Buriak, J. M. *Chem. Commun.* **1999**, 1051. (c) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. S.; Russell, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617. (d) Lu, X.; Lin, M. C. *Int. Rev. Phys. Chem.* **2002**, *21*, 137. (e) Bent, S. F. *J. Phys. Chem. B* **2002**, *106*, 2830. (f) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879.
- (2) Cheng, C. C.; Wallace, R. M.; Taylor, P. A.; Choyke, W. J.; Yates, J. T., Jr. *J. Appl. Phys.* **1990**, *67*, 3693.
- (3) Mayne, A. J.; Avery, A. R.; Knall, J.; Jones, T. S.; Briggs, G. A. D.; Weinberg, W. H. *Surf. Sci.* **1993**, *284*, 247.
- (4) Clemen, L.; Wallace, R. M.; Taylor, P. A.; Dresser, M. J.; Choyke, W. J.; Weinberg, W. H.; Yates, J. T., Jr. *Surf. Sci.* **1992**, *268*, 205.
- (5) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Zgierski, M. Z.; Wolkow, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 4532.
- (6) Hamers, R. J.; Hovis, J. S.; Lee, S.; Liu, H.; Shan, J. *J. Phys. Chem. B* **1997**, *101*, 1489.
- (7) Kiskinova, M.; Yates, J. T. *Surf. Sci.* **1995**, *325*, 1.
- (8) Liu, H.; Hamers, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 7593.
- (9) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 3548.
- (10) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 4082.
- (11) Ihm, J.; Cohen, M. L.; Chadi, D. J. *Phys. Rev. B* **1980**, *21*, 4592.
- (12) Wolkow, R. A. *Phys. Rev. Lett.* **1992**, *68*, 2636.
- (13) Pan, W.; Zhu, T. H.; Yang, W. T. *J. Chem. Phys.* **1997**, *107*, 3981.
- (14) (a) Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169. (b) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098.
- (15) Birkenheuer, U.; Gutdeutsch, U.; Rosch, N.; Fink, A.; Gokhale, S.; Menzel, D.; Trischberger, P.; Widra, W. *J. Chem. Phys.* **1998**, *108*, 9868.
- (16) (a) Cho, J. H.; Kleinman, L.; Chan, C. T.; Kim, K. S. *Phys. Rev. B* **2001**, *63*, 073306. (b) Cho, J. H.; Kleinman, L. *Phys. Rev. B* **2001**, *64*, 235420.
- (17) Miotto, R.; Ferraz, A. C.; Srivastava, G. P. *Surf. Sci.* **2002**, *507*, 12.
- (18) (a) Wang, G. T.; Mui, C.; Musgrave, C. B.; Bent, S. F. *J. Phys. Chem. B* **1999**, *103*, 6803. (b) Mui, C.; Bent, S. F. *J. Phys. Chem. A* **2000**, *104*, 2457.
- (19) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 11311.
- (20) Lu, X.; Xu, X.; Wang, N.; Zhang, Q.; Lin, M. C. *J. Phys. Chem. B* **2001**, *105*, 10069.
- (21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (22) For recent examples using the Si₉H₁₂ cluster model, see: (a) Konecny, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1999**, *121*, 7918. (b) Lu, X.; Lin, M. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4213. (c) Bacalzo-Gradden, F.; Lu, X.; Lin, M. C. *J. Phys. Chem. B* **2001**, *105*, 4368. (d) Lu, X.; Lin, M. C.; Zhang, Q. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2156. (e) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *New J. Chem.* **2002**, *26*, 160.
- (23) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785.
- (24) (a) Doren, D. J. *Adv. Chem. Phys.* **1996**, *95*, 1. (b) Hukka, T. J.; Pakkanen, T. A.; D'Evelyn, M. P. *J. Phys. Chem.* **1994**, *98*, 12420. (c) D'Evelyn, M. P.; Cohen, S. M.; Rouchouze, E.; Yang, Y. L. *J. Chem. Phys.* **1993**, *98*, 3560.
- (25) (a) Hovis, J. S.; Hamers, R. J.; D'Evelyn, M. P.; Russell, J. N., Jr.; Butler, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 732. (b) Hamers, R. J.; Hovis, J. S.; Greenlief, C. M.; Padowitz, D. F. *Jpn. J. Appl. Phys.* **1999**, *38*, 3879.
- (26) (a) Mezheny, S.; Lyubinetsky, I.; Choyke, W. J.; Wolkow, R. A.; Yates, J. T. *Chem. Phys. Lett.* **2001**, *344*, 7. (c) Lal, P.; Teplyakov, A. V.; Noah, Y.; Kong, M. J.; Wang, G. T.; Bent, S. F. *J. Phys. Chem. Phys.* **1999**, *110*, 10545. (c) Soreescu, D. C.; Jordan, K. D. *J. Phys. Chem. B* **2000**, *104*, 8259.

JA034779Z