

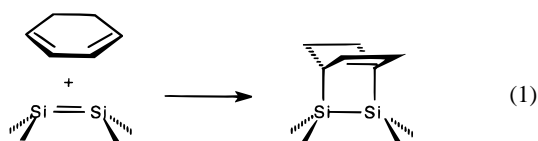
Theoretical Prediction of a Facile Diels–Alder Reaction on the Si(100)-2×1 Surface

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Received July 7, 1997

We describe theoretical studies of a novel reaction that can be used to form a molecularly defined, covalently bound organic film on the Si(100) surface. The method for creating this film is an analog of the well-known Diels–Alder reaction between a conjugated diene and a dienophile. In the example of eq 1, the dienophile is a surface dimer on the reconstructed Si(100)-2×1 surface. The bare surface dimer has two dangling bonds (one per surface atom) which are weakly coupled, as indicated by the π -bond in eq 1.



This [4 + 2] cycloaddition reaction on a silicon surface is novel in both synthetic and mechanistic terms. The reaction passivates surface dangling bonds by forming Si–C bonds, yet the product contains a C–C double bond which may prove useful in further controlled chemical reactions at the interface. If the Diels–Alder reaction occurs readily, it suggests new approaches to synthesis of molecular layers on dimer-reconstructed surfaces. The following paper¹ contains an experimental demonstration that this surface Diels–Alder reaction is the dominant product of adsorption for two conjugated dienes on Si(100). This reaction is mechanistically novel in being an example of reactive adsorption on Si(100) that may occur by a symmetric pathway. Simple orbital symmetry arguments show that dissociative adsorption of H₂ and the [2 + 2] addition of ethylene do not proceed on a symmetric pathway. Calculations of several dissociative adsorption reactions on ideal Si(100) surfaces all show that these reactions proceed through transition states in which the dimer is buckled.² In contrast, the Diels–Alder reaction is allowed to proceed on a symmetric path. While the dangling bonds are drawn as a π -bond in eq 1 (to emphasize the analogy with the traditional organic Diels–Alder reaction), dimers on the clean surface are not symmetric. Instead, the most stable surface structures have buckled dimers, with an asymmetric charge distribution between the two surface atoms. Because the energy difference between buckled and symmetric dimers is small, reactions may proceed along a symmetric path without incurring a large energy penalty for surface distortion.

As a prototype of the surface Diels–Alder reaction, we focus on the reaction of Si(100) with 1,3-cyclohexadiene (eq 1). Cyclohexadiene allows an uncomplicated theoretical analysis, since there is only one conformer and steric considerations suggest that the diene and surface can only react to form the

suprafacial [4s + 2s] product. The mechanism and energetics discussed for cyclohexadiene apply more generally, and we comment below on some reactions with other dienes. First-principles calculations³ based on the B3LYP hybrid Hartree–Fock/density functional method^{4,5} have been used to predict structures, energetics and vibrational frequencies of the products. This method generally gives accurate predictions of structures, bond energies, and gas phase reaction barriers.^{4,6–8} The surface is modeled as a cluster of nine Si atoms, with 12 subsurface bonds terminated by bonds to H atoms (Figure 1). The two atoms in the top layer represent the surface dimer; each has one dangling bond.

The calculations predict that the Diels–Alder addition product of 1,3-cyclohexadiene on Si(100)-2×1 (Figure 1a) is stable by 54.0 kcal/mol with respect to the reactants. The structural parameters (Table 1) show that the Si–Si σ bond is intact and the Si–C bond lengths are all typical. The six-member carbon ring has normal bond lengths and tetrahedral bond angles. The Si–Si–C bond angle is slightly compressed, but there is no evidence of significant ring strain in the system.⁹

Despite the substantial thermodynamic driving force for the Diels–Alder addition, one must be concerned that kinetic limitations may prevent the reaction from being observed. In particular, dienes can also react in a [2 + 2] addition to form a four-member ring product (Figure 1b). This competing reaction occurs readily for ethylene^{10,11} and should occur with little or no activation barrier for dienes as well. However, our calculations show that the [2 + 2] addition product is not as stable as the [4 + 2] product: the binding energy of the [2 + 2] product is only 38.8 kcal/mol. A hypothetical isomerization between the [2 + 2] and [4 + 2] addition products would be an isodesmic reaction, so the predicted energy difference between these structures of 15.2 kcal/mol is expected to be even more reliable than the binding energy of either structure. Thus, the [2 + 2] product is not likely to appear if the product distribution is thermodynamically determined. Group additivity arguments¹² would attribute the lower stability of the [2 + 2] product to strain in the four-member Si–Si–C–C ring. This strain is a consequence of the difference between Si–Si and C–C bond lengths. While the bond lengths in the [2 + 2] product show no evidence of strain (Table 1), the Si–Si–C bond angles are

(3) All calculations were done with the Gaussian94 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995. The results described for the reaction with 1,3-cyclohexadiene were obtained with the 6-31G** basis and the B3LYP functional (see refs 4 and 5). Full optimizations were done for all degrees of freedom in the cluster model, without constraints or symmetry (unless explicitly noted in the text). Frequency calculations were done for all critical points identified on the cyclohexadiene potential surface to verify that minima have no negative force constants and to test the order of the saddle point.

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(2) For a brief review, see: Doren, D. J.; Robinson Brown, A.; Konecny, R. In *Control of Semiconductor Surfaces and Interfaces*; Prokes, S. M., Glembocki, O. J., Brierley, S. K., Woodall, J. M., Gibson, J. M., Eds.; Materials Research Society: Pittsburgh, PA 1997; pp 45–50.

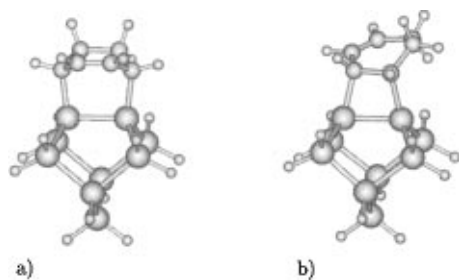


Figure 1. Structures of the cycloaddition products of the reaction of cyclohexadiene with the Si(100)-2 \times 1 surface. In a, the [4 + 2] adduct is shown with the C–C double bond in front, and in b, the [2 + 2] adduct is shown with the C₆ ring extending behind the dimer bond. The full Si₉H₁₂ cluster model is illustrated along with the adsorbed C₆H₈. The largest spheres are Si, the middle-size spheres are C, and the smallest are H.

Table 1. Selected Structural Parameters and Binding Energy for the [4 + 2] and [2 + 2] Adducts of Cyclohexadiene on Si(100)-2 \times 1 Calculated with the B3LYP Functional and 6-31G** Basis^a

	[4 + 2]	[2 + 2]
Si–Si	2.373	2.353
Si–C	1.953	1.965, 1.975
C–C	2.823 ^b	1.576
Si–C–C	109.7, 105.4	121.8, 110.0
Si–Si–C	96.6	78.1, 77.9
Si–C–H	110.5	111.9, 103.0
adsorption energy	54.0	38.8

^a Bond lengths in angstroms, bond angles in degrees, energy in kcal/mol. ^b Distance across the ring, between the two C atoms bound to Si atoms.

only 78°. A similar geometry has been seen in a molecular analog,¹³ where the low stability with respect to rearrangement is consistent with substantial ring strain.

While the Diels–Alder product is the thermodynamic product, the practical value of this reaction will be limited if it has a large kinetic barrier. To explore the kinetics of the [4 + 2] addition and to gain further insight into its mechanism, we have searched for a transition state to the reaction. Since the reaction is symmetry-allowed, we enforced C_s symmetry in this search. A saddle point was found corresponding to a barrier of only 0.3 kcal/mol. The geometry at the saddle is only slightly perturbed from that of the isolated reactants, yet minimizing the energy from the saddle point leads directly to the [4 + 2] addition product. The saddle point on the symmetric path is not a true transition state, but a second-order saddle point. Thus, there is another path from reactants to products (without C_s

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(14) Geometry optimization and frequency calculations on the [4 + 2] addition product of 2,3-dimethylbutadiene were done with the B3LYP functional and 6-31G* basis. This is a slightly smaller basis than the 6-31G** basis used in the reported results for cyclohexadiene, but the predicted structure and binding energy of the cyclohexadiene adduct are negligibly different with the two bases. As is typical of ab initio frequency calculations, there is a systematic error in the calculated frequencies which can be corrected by scaling. Using a scaling factor of 0.94 for all C–H stretch modes, we predict peaks at the following 10 frequencies (in cm⁻¹): 2846, 2847, 2850, 2854, 2885 (×2), 2916 (×2), 2958, 2976.

symmetry) of even lower energy, and 0.3 kcal/mol is a rigorous upper bound to the activation barrier. In other words, these calculations predict that any barrier to the reaction is too small to be chemically significant. Thus, the reaction should proceed via a concerted mechanism on either a symmetric or slightly asymmetric path without a significant activation barrier. No evidence for a stepwise radical mechanism was found.

The following paper reports some experimental tests of the predicted properties of these reactions using infrared spectroscopy.¹ To simplify analysis of the spectra, the reactions were attempted with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, which will react by the same mechanism as 1,3-cyclohexadiene. Our calculations predict that the geometry of the [4 + 2] addition products of these molecules is analogous to that of 1,3-cyclohexadiene, though the binding energies are somewhat stronger (67.5 kcal/mol for 1,3-butadiene and 64.9 kcal/mol for 2,3-dimethyl-1,3-butadiene). The observed spectra are consistent with the Diels–Alder product in both cases and inconsistent with significant formation of the [2 + 2] addition product. The vibrational spectrum was calculated for 2,3-dimethyl-1,3-butadiene to test the spectral assignments and aid in identifying the products.¹⁴ As shown in the following paper,¹ the calculated vibrational spectrum is in excellent agreement with the experimental observation. These experimental results provide strong evidence that the Diels–Alder reaction proceeds readily on Si(100), in agreement with the theoretical predictions presented here.

One significant difference between the Diels–Alder adducts of cyclohexadiene and butadiene is the steric interaction between adjacent surface sites. The [4 + 2] adduct of cyclohexadiene extends to both sides of the surface dimer bond, and it is large enough to prevent a second molecule from adsorbing at either of the adjacent sites in the same dimer row. The butadiene adduct lies on one side of the surface dimer, and two adjacent sites could be occupied without steric repulsion if both carbon fragments are oriented in the same sense. Such orientational ordering has been observed for [2 + 2] adducts of cyclopentene on Si(100).¹⁵

While some work has been done to develop solution chemistry for organic monolayer formation on Si(111),¹⁶ there are no comparable methods available for Si(100). Diels–Alder addition provides a new means for bonding organic materials to the Si(100) surface. This reaction may be useful in establishing covalently bound organic monolayers on Si, though it may be limited to applications in ultrahigh vacuum conditions. The presence of a C–C double bond in the adduct suggests the possibility of using the Diels–Alder reaction as an initial step in developing well-defined surface overlayers through a sequence of standard organic reactions to chemically modify the monolayer.

Acknowledgment. We wish to thank Dave Allara for suggesting that we study this reaction, and the National Science Foundation for support under grant no. CHE-9401312.

JA972247A

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