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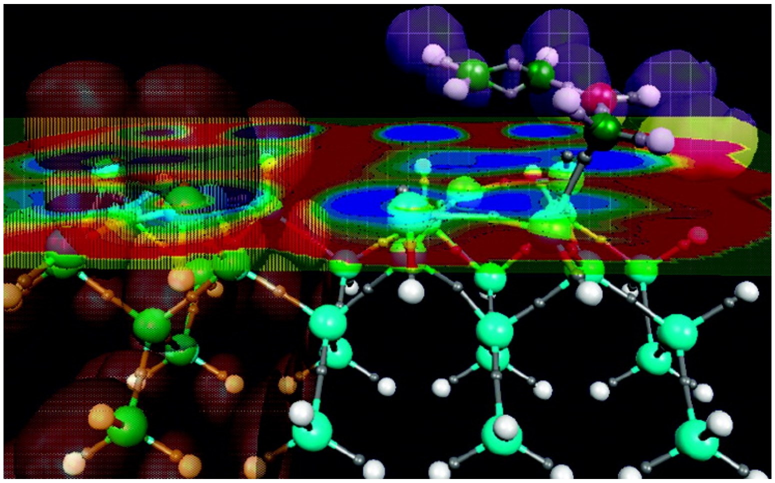
J. Am. Chem. Soc., **2005**, 127 (4), 1110-1111• DOI: 10.1021/ja046934v • Publication Date (Web): 08 January 2005



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Reaction Mechanism of *cis*-1,3-Butadiene Addition to the Si(100)-2 × 1 Surface

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The chemistry of hybrid structures composed of organic molecules and semiconductor surfaces is opening up exciting new avenues of development in molecular electronics, nanoscale devices, and surface lithography. Covalent attachment of organic molecules to such a surface can yield active devices, such as molecular switches or passive insulating layers. Moreover, the reactions can be controlled by tailoring specific organic molecules, suggesting possible new lithographic techniques. Despite recent experimental[1−4] and theoretical[5−7] investigations of the covalent attachment process, a detailed understanding of the chemistry is needed before it can be exploited for such novel purposes and is currently lacking.

The Si(100)-2 × 1 surface, one of the most commonly used surfaces for attachment of organic molecules, consists of parallel rows of silicon dimers, and it is well established experimentally[2,3] that these surface dimers can act as dienophiles, forming a [4 + 2] Diels−Alder (DA) adduct, or as an enophile to form a [2 + 2] adduct, the former being six-membered rings, with conjugated dienes.

Very recent scanning tunneling microscopic (STM) experiments[4] of 1,3-cyclohexadiene addition to the surface show that, in addition to the DA [4 + 2] adduct, other products are possible, specifically, [4 + 2]-like adducts that bridge two dimers within a row or two dimers in adjacent rows and two intradimer [2 + 2] adducts. Finally, a sixth species was also reported, although it was not possible to determine its identity conclusively.

Despite the novelty of these results, neither experiments nor static ab initio calculations can identify specific mechanisms by which these addition products form. For the DA [4 + 2] adduct, an outstanding and controversial question of whether the reaction mechanism involves a concerted (symmetric or asymmetric) or stepwise formation of the two Si−C bonds remains unanswered; one might expect that similar questions arise for the other adducts.

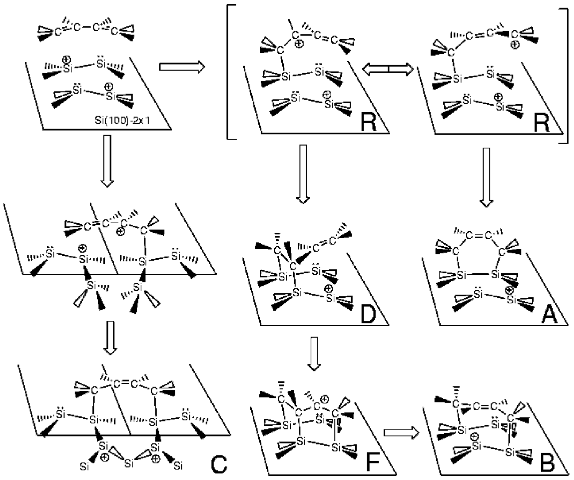
To address these issues, we have undertaken a finite temperature ab initio molecular dynamics (AIMD) study, using forces obtained "on the fly" from electronic structure calculations, to investigate the addition product distribution as well as the underlying mechanistic aspects of the reaction.

AIMD calculations were performed using the PINY_MD code[8] on a system of four silicon layers composed of 32 atoms (four surface dimers), a passivating bottom layer of hydrogens, and one *cis*-1,3-butadiene at a temperature of 300 K. The electronic similarity between 1,3-butadiene and the 1,3-cyclohexadiene of ref 4 allows direct comparison between theory and experiment. The electronic structure was represented within the generalized gradient[9] formulation of Kohn−Sham density functional theory (DFT). The orbitals were expanded in a plane-wave basis at the Γ-point, with atomic pseudopotentials,[10] up to a cutoff of 35 Ry, which is sufficient to converge the geometry of the butadiene and reproduce the change in energy per surface dimer upon reconstruction.[11] Rigorous treatment of the surface boundary conditions[12] allowed a box with periodic dimensions 15.34 Å, 7.67 Å, and nonperiodic dimension 22.53 Å to be used. The dynamics of the system was generated using a new formulation[11] of the Car−Parrinello algorithm[13] for treating reactive systems.

Table 1. Distribution of the Final Addition Products[17]

product	theory (%)	expt (%)	product	theory (%)	expt (%)
A	15	11 ± 3	D(+E)	30	22 ± 15
B	30	31 ± 6	H	10	21 ± 5
C	15	16 ± 7			

Scheme 1. Mechanism of Addition Product Formation



Since the geometry and charge distribution of the neat Si(100)-2 × 1 surface can influence the reaction mechanism, it is necessary to review our current understanding of the surface. The present theoretical approach, in agreement with recent experiments,[14] indicates that the room-temperature structure is the c(4 × 2) buckled dimer structure, which persists to temperatures as low as 10 K.[14] The average geometry of the dimers is found to be in good agreement with static ab initio calculations.[15,16] Consequently, the charge distribution within each dimer is asymmetric, with an excess positive and negative charge on the lower and upper atoms, respectively.

To have a meaningful product distribution, 40 trajectories, each of length 2 to 3 ps, were initiated from an unbiased distribution of initial configurations of the butadiene above the surface. In total, nearly 110 ps of trajectory data were generated. Table 1 shows the percentages of the addition products[17] (see Scheme 1) together with the experimental[5] values for 1,3-cyclohexadiene. It can be seen that the yields of all products analogous to those of ref 4, that is, A−D(+E), agree with experiment within the error bars. Some slight differences between the 1,3-butadiene and 1,3-cyclohexadiene products are: (1) for the former, the B adduct forms diagonally across two intrarow dimers and (2) the [2 + 2] adduct is actually an interdimer [2 + 2]-like adduct within a row.

10.1021/ja046934v CCC: $30.25

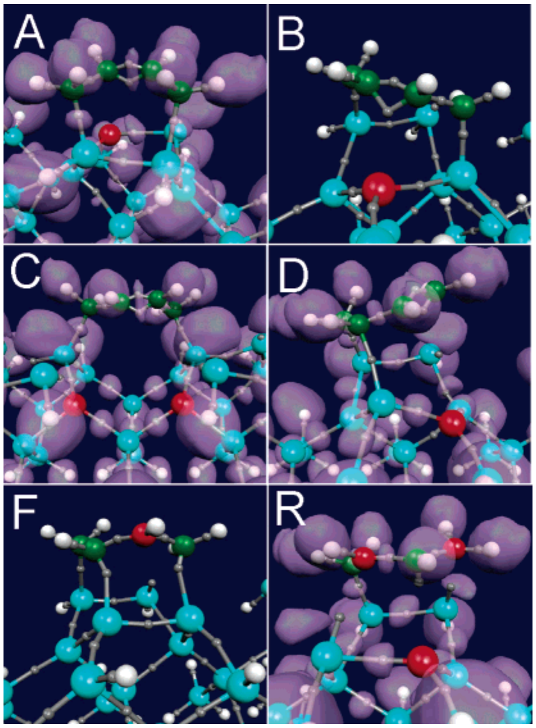


Figure 1. Snapshots of the addition products obtained. The lettering corresponds to that of Scheme 1. Blue, green, and white spheres denote Si, C, and H atoms, respectively, and gray spheres indicate the location of Wannier centers. Red spheres locate atoms with positive full or partial charge. Full positive charge is defined to be an atom surrounded by three Wannier centers. The purple surface is the ELF 0.95 isosurface.

Despite the variety of addition products, a detailed electronic structure analysis of the trajectories reveals that a common mechanism underlies their formation (see Scheme 1). The scheme presented is supported by electron localization function (ELF)[18] isosurfaces, which use a conditional probability to locate spatial regions of high electron density (Figure 1). Figure 1 also shows the centers of maximally localized Boys−Wannier orbitals.[19]

The common mechanism (Scheme 1) begins with a nucleophilic attack of the C═C double bond on the positive member of a Si−Si surface dimer, suggesting a predominantly stepwise mechanism. The subsequent migration of the local positive charge from the Si atom, now neutralized by formation of the Si−C bond, dictates the subsequent fate of the reaction. In all cases, the next step involves the migration of the positive charge into the butadiene, leading to a carbocation (Scheme 1R). Carbocation formation has also been observed in STM measurements of ethylene on the Si(100)-2 × 1 surface.[20] The carbocation, which can exist for up to 1 to 2 ps, is stabilized by resonance, as illustrated by the three ELF lobes and three Wannier centers around the positive carbon atoms (indicated by red spheres; Figure 1R). The Wannier center of the delocalized orbital is located below the middle carbon atom, indicating that it is shared by two bonds. Since the carbocation bonds to an Si atom of a surface dimer and the other dimer member has a net negative charge, an intermediate zwitterionic state ensues. In one of the resonant structures, the positive charge is “localized” on the end of the butadiene (Scheme 1R-right), which allows the carbon to attack the negatively charged Si atom, leading to the final DA [4 + 2] adduct (Figure 1A, Scheme 1A).

If the double bond is localized on the end of the butadiene (Scheme 1R-right), then the positive carbon can attack the negatively charged Si of a neighboring dimer, leading to an inter-row [2 + 2]-like adduct (Figure 1D, Scheme 1D). The trajectories indicate a further reaction that occurs when the butadiene is oriented so as to allow a second nucleophilic attack on the positively charged Si of this dimer. The reaction involves an intermediate “fluxional” species (Figure 1F, Scheme 1F) that rapidly converts into a stable [4 + 2]-like interdimer adduct (Figure 1B, Scheme 1B) via an electron pair reorganization. The existence of such a “fluxional” species was also suggested in ref 4. The [2 + 2]-like adduct, D, is stabilized if the double bond at the end of the butadiene is oriented between the rows. Finally, the inter-row adduct formation is initiated by a second nucleophilic attack of the C═C double bond in the zwitterion on the positively charged Si atom in a neighboring row. Here, a nine-membered ring finally forms, leading to a migration of positive charge into a bulk layer, as seen in the ELF (Figure 1C, Scheme 1C).

The preceding discussion highlights the predominance of an stepwise zwitterionic mechanism governing addition product formation on the Si(100)-2 × 1 surface. Although we cannot rule out a concerted mechanism, one might expect on statistical grounds that the initially asymmetric charge distribution in the surface dimers allows only very special initial conditions to lead to a concerted reaction path. This suggests that the mechanism of the Diels−Alder adduct formation is dominated by a nonconcerted mechanism[21] (Scheme 1), thus addressing one of the long-standing questions concerning this reaction.

Acknowledgment. This work was supported by NSF Grants CHE-9875824 and CHE-0310107 and the Camille and Henry Dreyfus Foundation.

Supporting Information Available: Results from spin-unrestricted AIMD, **k**-point calculations, and other details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA046934V