Reaction Pathway of the [4 + 2] Diels−Alder Adduct Formation on Si(100)-2×1

Peter Minary and Mark E. Tuckerman*

Department of Chemistry, New York University, New York, New York 10003

Received June 11, 2004; E-mail: mark.tuckerman@nyu.edu

Despite a long history of experimental[1,2] and theoretical[3] investigation, the mechanism of the Diels−Alder (DA) reaction has been controversial since its discovery 80 years ago. The subject of the debate has focused on two competing alternative pathways: (i) a concerted mechanism in which the transition state (TS) is formed in one step either simultaneously (synchronous path) or sequentially (asynchronous path); (ii) a stepwise (nonconcerted) mechanism, involving forming either a diradical or a zwitterion as an intermediate state (IS).

Recent theoretical and experimental studies[4−6] identified a novel DA-type addition reaction between a conjugated diene and the Si(100)-2×1 surface, predicting the [4 + 2] DA adduct as the major product of this reaction. Another recent experiment[7] showed that other [4 + 2] adducts can form on the surface as well as a small percentage of [2 + 2] adducts. These new findings are particularly promising as novel covalent attachment techniques of hydrocarbons on silicon are generating exciting new inroads into molecular electronics and nanoscale devices, surface lithography, and nanotechnology.

Despite the novelty of these results, neither experiments nor static ab initio calculations can identify specific mechanisms by which the addition products form. Recently, we reported on a theoretical study probing the common mechanistic features of the distribution of addition products.[8] Here, we employ similar theoretical techniques to investigate the detailed reaction pathway leading to the [4 + 2] DA adduct on the Si(100)-2×1 surface.

Our studies employ ab initio molecular dynamics (AIMD), in which forces are generated "on the fly" from electronic structure calculations. All calculations were carried out using the PINY_MD code[9] on a system of four silicon layers composed of 32 atoms (four surface dimers), a passivating bottom layer of hydrogens, and one 1,3-butadiene molecule at a temperature of 300 K. The electronic structure was represented within the generalized gradient[10] formulation of Kohn−Sham density functional theory (DFT). Electronic orbitals were expanded in a plane-wave basis, with atomic pseudopotentials,[11] up to a 35 Ry cutoff, which is sufficient to converge the geometry of the butadiene and reproduce the change in energy per surface dimer upon reconstruction.[12] Rigorous treatment of the surface boundary conditions[13] allowed a box with periodic dimensions 15.34, 7.67, and nonperiodic dimension 22.53 Å to be used. The dynamics of the system were generated using a new formulation[12] Car−Parrinello algorithm[14] for treating reactive systems.

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,[15] indicates that the room-temperature structure is the c(4×2) buckled dimer structure, which persists to temperatures as low as 10 K.[15] The average geometry of the dimers is found to be in good agreement with static ab initio calculations.[16,17] Consequently, the

Scheme 1. Mechanism of Addition Product Formation
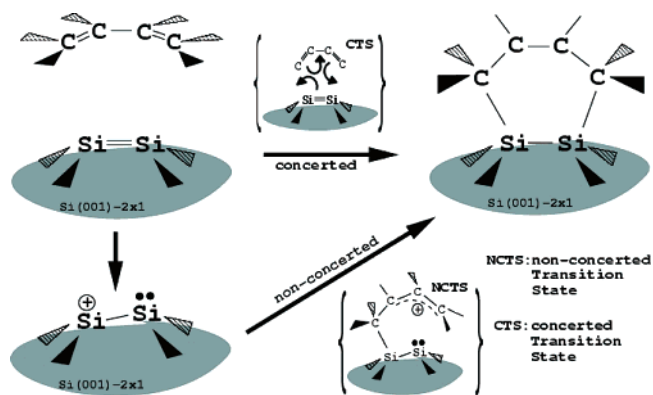
charge distribution within each dimer is asymmetric, with an excess positive and negative charge on the lower and upper atoms, respectively.

Scheme 1 depicts the possible reaction mechanisms between butadiene and the Si(100)-2×1 surface leading to the DA [4 + 2] adduct. In a concerted one-step mechanism, (Si$_1$−C$_1$) and (Si$_2$−C$_4$) bonds form simultaneously in either a synchronous or an asynchronous pathway. The former implies an unbuckling of a surface dimer during the reaction and/or a negligible charge asymmetry within a dimer. A nonconcerted stepwise mechanism involving a zwitterionic intermediate is also depicted in Scheme 1. This type of path involves formation of a positively charged carbocation bonded to a negatively charged Si−Si dimer.

To investigate the thermodynamic reaction path of the DA [4 + 2] adduct formation, the free energy profile $\Delta G(\xi)$, where ξ is an appropriately chosen reaction coordinate, is determined. Here, ξ is taken to be the relative coordinate between the mass centers of the two outer carbons of the 1,3-butadiene and the two Si atoms in the dimer forming the adduct, $\xi = \xi(\mathbf{r}) = \frac{1}{2}|(\mathbf{r}_{Si_1} + \mathbf{r}_{S_2}) - (\mathbf{r}_{C_1} + \mathbf{r}_{C_4})|$. ξ decreases from 3.90 to 1.96 Å as the butadiene approaches the surface and forms the DA adduct. The free energy profile is then computed via thermodynamic integration via

$$\Delta G(\xi) = \int_{\xi_0}^{\xi} d\xi' \langle \partial H/\partial \xi' \rangle_{cond} \qquad (1)$$

where $H = H(\mathbf{r},\mathbf{p};\xi)$ is the Hamiltonian of the system, and $\langle \cdots \rangle_{cond}$ is a conditional average over an equilibrium ensemble at a fixed value of ξ.[18] To enhance sampling along the path, the average in eq 1 was performed using the blue moon ensemble method,[19] which reformulates eq 1 in terms of constraints $\xi(\mathbf{r}) = \xi'$ and $\dot{\xi}(\mathbf{r},\dot{\mathbf{r}}) = 0$. To compute the profile, 13 separate systems were set up with ξ values equidistantly distributed along the [1.97 Å, 3.90 Å] interval, and production runs of 8 ps in length were carried out after a 1.0 ps equilibration period at each point, for a total of 117 ps.

The free energy profile (Figure 1) shows a deep minimum corresponding to the final DA product and a plateau at $\xi = 2.75$
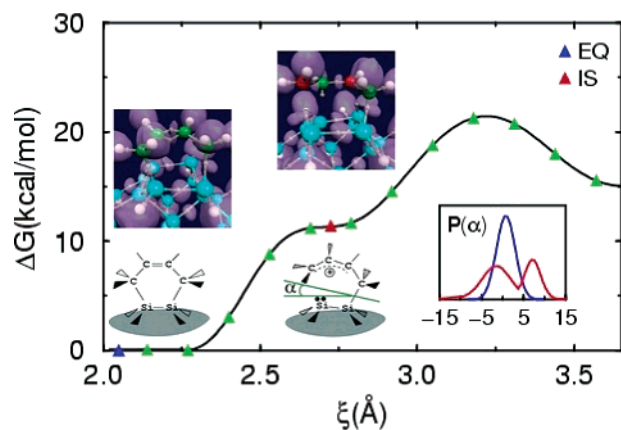
Figure 1. Free energy along the reaction pathway leading to a Diels−Alder [4 + 2] adduct. Blue and red triangles indicate the product (EQ) and intermediate states (IS), respectively. Inset shows the buckling angle (α) distribution of the Si dimer for both the IS (red) and the EQ configurations (blue). The snapshots include configurations representing the IS and EQ geometries. Blue, green, and white spheres denote Si, C, and H atoms, respectively, and gray spheres indicate the location of Wannier centers. Red spheres locate positively charged atoms. The purple surface is the ELF 0.95 isosurface.

Å, implying a short-lived intermediate state. If the mechanism were concerted, one would expect a profile with a single minimum, corresponding simply to the final product state. The profile in Figure 1 is clearly more characteristic of a nonconcerted mechanism involving a well-defined reaction intermediate. That the free energy barrier is relatively low (3−4 kcal/mol) suggests that the reaction can occur at room temperature.

Direct investigation of the mechanism was carried out by studying 40 trajectories, each of length 2−3 ps (for a total of 110 ps), initiated from an unbiased distribution of initial configurations of the butadiene above the surface. Detailed analysis of 10 trajectories that formed the [4 + 2] DA adduct as the final product indicates a dominant mechanism, which begins with a nucleophilic attack of the C=C bond on the positive end of a Si−Si surface dimer. The next step involves the migration of the excess positive charge into the butadiene, leading to carbocation formation, consistent with STM measurements of ethylene on the Si(100)-2×1 surface.[22] Evidence for the carbocation is provided by the electron localization function (ELF) isosurface,[20] which uses a conditional probability to locate spatial regions of high electron density (see Figure 1), as well as the centers of maximally localized Boys−Wannier orbitals.[21] The dearth of electron density around the red carbon indicates a net local positive charge. Further evidence is provided by the time trace of the Si−C and C−C bond lengths in the butadiene for a representative trajectory (see Figure 2). There is a brief time interval in which the two Si−C distances become distinctly different, as only one Si−C bond is formed. Moreover, Figure 2 clearly shows the interchange of CC single and double bonds as the DA adduct is formed. Furthermore, at its maximum value, $d[C_3−C_4] = d(s)$ ($d(s)$ is the single bond length) and $d[C_1−C_2] = d[C_2−C_3] = d(s − d)$ ($d(s) < d(s − d) < d(d)$) suggesting a possible resonant structure (see Scheme 1) that could help stabilize the carbocation.

The preceding discussion highlights the predominance of a nonconcerted zwitterionic mechanism governing DA [4 + 2] adduct 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.
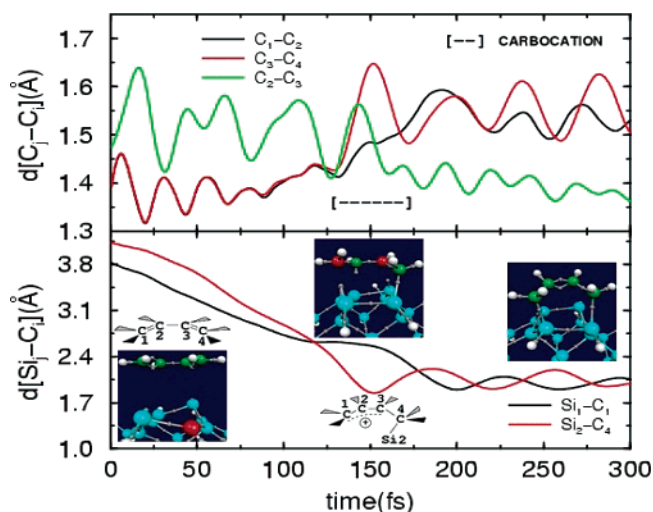

Figure 2. Si−C and C−C bond lengths vs simulation time for a representative trajectory leading to the [4 + 2] Diels−Alder adduct. From left to right the three snapshots depict: (i) butadiene above the Si(100)-2×1 surface, (ii) carbocation formation, (iii) final [4 + 2] DA adduct. Sphere coloring is the same as in Figure 1.

Supporting Information Available: Results from spin-unrestricted AIMD calculations which address a possible diradical mechanism. This material is available free of charge via the Internet at http://pubs.acs.org

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