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Competing Mechanisms in the Optically Activated Functionalization of the Hydrogen-Terminated Si(111) Surface

Yosuke Kanai* and Annabella Selloni*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received December 22, 2005; E-mail: ykanai@princeton.edu; aselloni@princeton.edu

The organic functionalization of semiconductor surfaces is a promising route for the development of organic−inorganic devices and molecular nanostructures.[1] In particular, over the past few years, much attention has been focused on the formation of covalently attached monolayers on silicon, starting from hydrogen-terminated Si (H−Si) surfaces.[2] On extended H−Si surfaces, a radical chain reaction mechanism is widely believed to be operative when a Si dangling bond is initially present, for example, created by the tip of a Scanning Tunneling Microscope or by UV irradiation. Instead, the mechanism is not as clear for the case where visible light with $h\nu < 3.5$ eV (the energy required to cleave a Si−H bond) is used to activate the reaction on a fully H-saturated surface. Such a "mild" functionalization procedure, which is particularly important for the attachment of biomolecules, was initially developed by Stewart and Buriak on porous silicon (p-Si)[3] and has been more recently extended to well-defined H−Si(100) and H−Si(111) surfaces by Zuilhof and co-workers.[4−6] On both p-Si and extended H−Si surfaces, the initial step of the optically activated reaction is believed to be the nucleophilic attachment of the terminally unsaturated molecule, involving surface-localized holes induced by the excitation. However, while for p-Si this initial step is followed by the abstraction of a H atom from the SiH unit at the *same attachment site* (Path A),[3,7] recent experiments suggest that on H−Si surfaces the nucleophilic attachment is followed by the capture of a hydrogen from a *neighboring SiH unit* (Path B). Discrimination between these two mechanisms is important for understanding the growth and characteristics of the organic adlayer. With Path A, the growth would proceed through a sequence of identical, uncorrelated molecular attachment events. Path B, instead, would lead to a surface Si dangling bond (DB), which then acts as an initial site for the following surface radical chain reaction.[5,6]

In this Communication, we theoretically investigate these two competing mechanisms in the attachment of an alkene (butene) and an aldehyde (propanaldehyde) on H−Si(111), using the recently introduced First Principles String Molecular Dynamics (FPSMD),[8] which combines DFT-based First Principles Molecular Dynamics (FPMD)[9] with the string method[10] for finding reaction pathways. As described in ref 7, we model the photoexcited system by assuming it to be in its lowest excited state, with spin triplet character (the ground state is a spin singlet). This is a reasonable assumption considering (*a*) the very fast phonon-mediated relaxation (<1 ps) and equally fast spin relaxation time expected at room temperature; (*b*) the considerably long recombination time of both the H−Si(111) surface (∼microseconds) and the molecule in its triplet excited state (∼milliseconds).[11] Since DFT is formally exact for the lowest energy state of each spin multiplicity, our approach is well suited for describing the lowest triplet excited state. We employed the PBE[12] exchange-correlation functional, and the triplet excited state ($S = 1$) was treated by performing spin-polarized calculations with $S_Z = 1$.

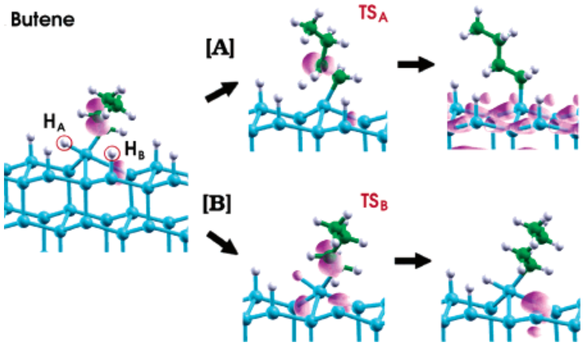

Figure 1. Geometries and spin densities of relevant states along Path A and Path B for butene on H−Si(111). Left, intermediate metastable state (IMS); middle, transition states (TS); right, final states. The 0.01 au spin density isosurface is shown in all cases, except for the final state of Path A, where the spin density is highly delocalized and shown with isosurface of 0.001 au.

The surface was modeled using a periodically repeated supercell containing a slab with six Si layers and eight Si atoms/layer. Both surfaces of the slab were terminated by H atoms. The FPSMD[8] approach was used to obtain the minimum energy paths (MEPs) for the reactions. Further details are given in the Supporting Information.

We start by considering the attachment of the terminally unsaturated molecule, butene, on H−Si(111). While no adsorption is found to take place in the lowest singlet ($S = 0$) state, a metastable adsorbed state—that is, a local minimum in the Potential Energy Surface (PES) of the molecule−surface system—is obtained when $S = 1$, with energy 2.18 (∼1.06) eV *above* that of the *noninteracting* molecule−surface singlet ground state (lowest triplet state, corresponding to surface and molecule in the triplet excited and singlet ground states, respectively). This result suggests that the nucleophilic attachment of the molecule should occur before complete relaxation of the photoexcited electron−hole (e−h) pair in the Si conduction/valence bands, as indeed indicated by experiments.[6] In the Intermediate Metastable State (IMS), the bonding environment of the surface Si atom that is pentacoordinated with the adsorbed molecule becomes highly distorted[6] (see Figure 1); in particular, one of the three back-bonds of this surface Si atom becomes much longer (by 0.6 and 0.2 Å for butene and propanaldehyde, respectively) and weaker, while correspondingly the bond with the H$_A$ atom in Figure 1 becomes stronger. In addition, a significant spin density ($\sigma(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$) at the radical carbon atom is present. Analysis of the PDOS in Figure 2 shows that most of this spin density originates from the orbital where the photoexcited electron resides. Thus relaxation of the photoexcited electron from the Si conduction band to this state appears to be essential for the build-up of the spin density at the radical C atom, which is responsible for the H atom abstraction.

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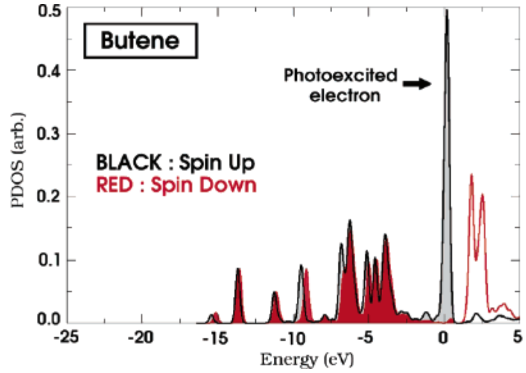

Figure 2. Projected density of states (PDOS) onto the 2p orbitals of the radical carbon atom for the IMS of butene on H−Si(111). The energy zero corresponds to the top of the valence band of unexcited H−Si(111). Occupied states are shaded.

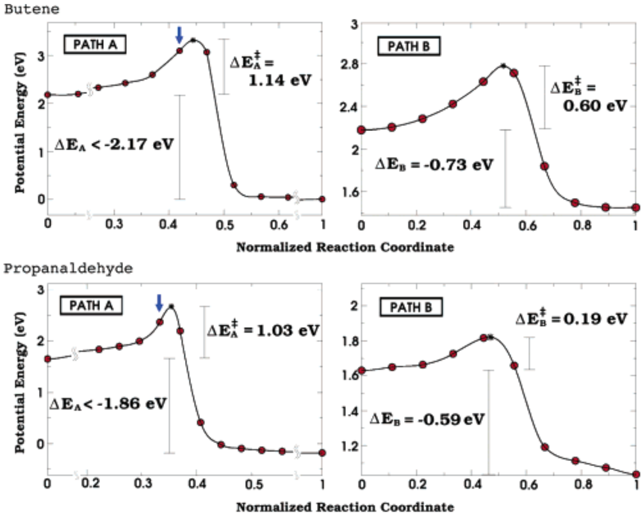

Figure 3. Potential energy profiles along the MEPs of Paths A and B for butene (top) and propanaldehyde (bottom). The energy zero corresponds to noninteracting surface and molecule in the singlet ground state. The blue arrow indicates the state at which the effect of relaxation to the $S = 0$ PES was studied (see text).

Table 1. Energies (in eV) of Relevant States along Paths A and B[a]

	IMS	Path A		Path B	
		TS	final	TS	final
		Alkene			
$S = 1$	2.18	3.32	<0.01	2.78	1.45
$S = 0$	2.44	2.38	−1.08	2.49	1.94
		Aldehyde			
$S = 1$	1.63	2.66	<−0.23	1.82	1.04
$S = 0$	1.45	1.94	−1.31	1.78	1.35

[a] Lowest triplet ($S = 1$) and singlet ($S = 0$) energies, *both at the triplet state geometry*, are reported. All energies are referred to the singlet ground state ($S = 0$) of the noninteracting surface−molecule system.[14]

Once in the IMS, the molecule can either desorb or abstract a H atom according to one of the above-mentioned Path A and Path B mechanisms. For molecular desorption on the lowest triplet PES, we find a barrier (exothermicity) of 0.79 (∼1.06) eV for butene and 0.15 (∼0.52) eV for propanaldehyde. Turning next to the H-abstraction reactions, the potential energy profiles along the calculated Paths A and B MEPs are shown in Figure 3. It appears that the reactions are exothermic in both pathways but to a very different extent; notably the final state along Path A is much lower in energy (see also Table 1). On the other hand, the reaction barrier for Path A is considerably higher than that for Path B, by more than 0.5 (0.8) eV for the alkene (aldehyde) molecule. Such a large barrier for Path A, which is related to the local structural distortions highlighted above, is consistent with recent theoretical results for Si quantum dots (QD), showing that the barrier for this process increases with increasing QD size.[7]

Thus, while Path A is thermodynamically favored, its significantly larger barrier can limit its viability. To confirm this point further, we also considered whether relaxation to the spin singlet state could favorably affect H abstraction via Path A. We carried out FPMD simulations on the singlet PES starting from a few atomic geometries along the MEPs for Path A in Figure 3. In particular, we considered cases in which relaxation to the $S = 0$ state takes place while "climbing" toward TS_A, at points significantly higher in energy than TS_B, so that the H_B atom could have been abstracted before reaching these points. In all these cases, we observed desorption of the molecule from the surface, with no H abstraction taking place (see also the Supporting Information). Thus, our calculations confirm that on H−Si(111) H_A abstraction has a much higher activation energy than the abstraction of H_B, even when the possibility of e−h recombination is considered. Once the DB is created via Path B, the radical chain reaction can readily take place as observed experimentally[5,6] and discussed previously.[13,15]

In conclusion, our calculations indicate that the optically activated functionalization of extended H−Si surfaces should occur via Path B. This is at variance with the case of p-Si and Si QDs, where the alternative Path A, involving H abstraction at the attachment site, appears to be operative.

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Supporting Information Available: Geometries on reaction paths and PDOS for propanaldehyde. Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *150*, 413−441.
(2) (a) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **2000**, *406*, 48−51. (b) Wayner, D. D. M.; Wolkow, R. A. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 23−34. (c) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271−1308.
(3) Stewart, M. P.; Buriak, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 7821−7830.
(4) Sun, Q.; de Smet, L. C. P. M.; van Lagen, B.; Wright, A.; Zuilhof, H.; Sudhölter, E. J. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1352−1355.
(5) Eves, B. J.; Sun, Q.; Lopinski, G. P.; Zuilhof, H. *J. Am. Chem. Soc.* **2004**, *126*, 14318−14319.
(6) Sun, Q.; de Smet, L. C. P. M.; van Lagen, B.; Giesbers, M.; Thüne, P. C.; van Engelenburg, J.; de Wolf, F. A.; Zuilhof, H.; Sudhölter, E. J. R. *J. Am. Chem. Soc.* **2005**, *127*, 2514−2423.
(7) Reboredo, F. A.; Schwegler, E.; Galli, G. *J. Am. Chem. Soc.* **2003**, *125*, 15243−15249.
(8) Kanai, Y.; Tilocca, A.; Selloni, A.; Car, R. *J. Chem. Phys.* **2004**, *121*, 3359−3367.
(9) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471−2474.
(10) Weinan, E.; Ren, W.; Vanden-Eijnden, E. *Phys. Rev. B* **2002**, *66*, 1−4.
(11) (a) Goldman, J. R.; Prybyla, J. A. *Phys. Rev. Lett.* **1994**, *72*, 1364−1367. (b) Yablonovitch, E.; Allara, D. L.; Chang, C. C.; Gmitter, T.; Bright, T. B. *Phys. Rev. Lett.* **1986**, *57*, 249−252. (c) Webb, L. J.; Lewis, N. S. *J. Phys. Chem. B* **2003**, *107*, 5404−5412.
(12) Perdew, J. P.; Burke, K.; Ernzerholf, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.
(13) (a) Takeuchi, N.; Kanai, Y.; Selloni, A. *J. Am. Chem. Soc.* **2004**, *126*, 15890−15896. (b) Kanai, Y.; Takeuchi, N.; Car, R.; Selloni, A. *J. Phys. Chem. B* **2005**, *109*, 18889−18894.
(14) The uncertainty in the final state energy along Path A is due to the delocalized nature of the spin density in this state. However, this uncertainty does not affect our analysis and conclusions.
(15) However, for propanaldehyde, molecular desorption has a slightly lower barrier than H_B abstraction, suggesting that an optically activated functionalization for the formation of alkoxyl monolayers may not be as effective as that for forming alkyl monolayers on Si(111).

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