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Azide Reactions for Controlling Clean Silicon Surface Chemistry: Benzylazide on Si(100)-2 × 1

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With the recent advances in using molecular assemblies for electron transfer in lateral direction with respect to semiconductor surfaces,[1,2] the chemistry that can selectively and cleanly deliver aromatic compounds to the single crystal silicon surfaces has become of the utmost importance. Despite the fact that multiple surface features have already been produced by defect-induced or STM-induced chemistry, and despite the fact that formidable evidence exists for a set of very attractive properties based on self-assembly of aromatic molecules on Si(100)-2 × 1, the chemical toolbox that allows one to form such assemblies is incredibly limited. Traditional silicon surface attachment chemistry also has a limited potential because of the high reactivity of the silicon surface and difficulty controlling the chemistry of multiply functionalized molecules. At the same time, some of the most potent chemical transformations are based on oxygen-containing functional groups, which pose an additional burden because of the subsurface oxygen migration.[3−5]

One of the most intriguing approaches to delivering aromatic compounds onto a semiconductor substrate can be based on the azide chemistry.[6] In fact, previous studies of hydrazoic acid, HN_3, on Si(100)-2 × 1 proved that azide attachment followed by the nitrogen elimination can be conducted in ultrahigh vacuum cleanly, without oxidation of the surface.[7,8] Here we report the first confirmed investigation using a combination of experimental and computational methods of the azide chemistry on a Si(100) that delivers an organic group with an aromatic ring in a clean and selective manner, with a single attachment product. The elimination of a N_2 molecule produces a stable adduct on a Si(100)-2 × 1 surface. Similar chemistry can further be used with different alkyl and aryl substituents to produce the desired surface features based on assemblies of molecules. In fact, it is expected that phenylazide, PhN_3, will provide the most robust surface features with tight overlap of π-orbitals, without oxygen incorporation.[6] However, one of the difficulties with handling phenylazide is the fact that it is explosive under distillation conditions. Thus, all the chemistry relevant for the future modification of the Si(100)-2 × 1 surface will be summarized here based on a less reactive benzylazide, $PhCH_2N_3$, and can be applied in the future to phenylazide and essentially any other aromatic hydrocarbons. This general approach also suggests that varying the linker group between the azide function and the aromatic system will allow for varying the overlap of the π-systems of the aromatic rings and adding one more handle to controlling the specific arrangement of surface adducts.

The mechanism of azide reactions with unsaturated entities has been a subject of a debate for several decades.[9] It was suggested in a theoretical investigation that, on the Si(100)-2 × 1 surface, methylazide should react via a concerted 1,3-cycloaddition with no noticeable barriers and should ultimately lead to a stable surface adduct with a Si−Si−N cycle.[6] On the basis of the previous experimental studies of hydrazoic acid,[7,8] it can be concluded that the final product of an azide interaction with a Si(100)-2 × 1 surface is indeed similar to the one proposed theoretically. However, as the theoretical approach showed no barrier for the addition of methylazide to this surface and no intermediates leading to the product of 1,3-cycloaddition, practical importance of this reactive chemistry would be diminished since it would be difficult to control the reactions. Our detailed investigation of the benzylazide reaction pathways is summarized in Figure 1.

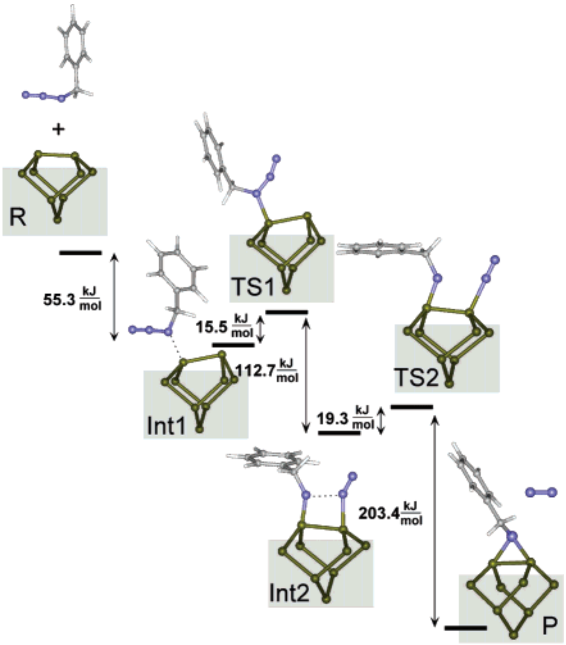

Figure 1. Surface reaction pathways for the interaction of benzylazide with a Si(100)-2 × 1 surface represented by a Si_9H_{12} cluster. Computations were performed at the B3LYP/6-311+G(d,p) level of theory. Hydrogen atoms representing silicon cluster termination are omitted for clarity. Green, silicon; blue, nitrogen; gray, carbon; white, hydrogen.

Here, the B3LYP/6-311+G(d,p) computational method was used to simulate in detail the adsorption configurations of benzylazide on a silicon surface modeled by a single dimer Si_9H_{12} cluster. The silicon atoms representing the subsurface were not fixed at any particular positions in this investigation. However, since all the chemistry described here essentially involves only the top two atoms of the silicon dimer, it is not expected that fixing the subsurface silicon atoms in this model would affect the predicted binding energies or the transition states. In fact, a very detailed recent study of nitrobenzene on Si(100)-2 × 1 suggested that this effect would be negligibly small.[5]

Instead of a barrierless addition leading to the 1,3-adduct proposed previously for methylazide,[6] benzylazide forms a stable, albeit a weakly bound adduct, Int1, with the Si(100)-2 × 1 surface. Multiple other reaction pathways following the weak adsorption have also been considered, and the exact assignments are a subject

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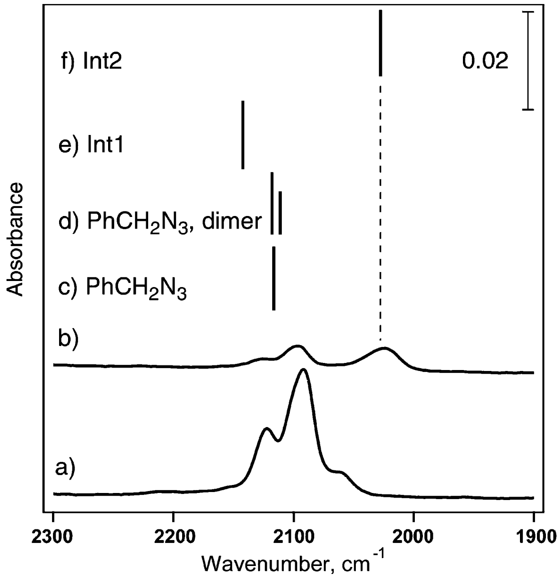

Figure 2. Infrared studies of benzylazide on Si(100)-2 × 1: (a) 1 L submonolayer coverage condensed on a clean Si(100)-2 × 1 surface at 100 K; (b) same as (a) but briefly annealed to 160 K; (c) predicted infrared spectrum for a single molecule of benzylazide in a gas phase; (d) predicted infrared spectrum for a dimer of benzylazide (with computationally predicted relative intensities); (e) predicted infrared spectrum for Int1; (f) predicted infrared spectrum for Int2. All spectra are obtained at the B3LYP/6-311+G(d,p) level of theory, and the frequencies are scaled by 0.95. The spectra corresponding to the adsorbed benzylazide are reported with a deuterium-substituted silicon cluster to avoid interference from Si−H vibrations.

of a separate publication. However, a combination of experimental and computational studies suggests that there is indeed a stable configuration for adsorption of benzylazide on a Si(100)-2 × 1 surface. Following this weak chemisorption, the surface process leads to the formation of a stable surface intermediate with the N_2 stabilized by the presence of the $NCH_2C_6H_5$ group, Int2, which eventually releases N_2 into the gas phase and forms the final product.

This computational analysis provides a useful alternative to the 1,3-cycloaddition, especially that the intermediates involved can be trapped on a surface and identified spectroscopically. This theoretical prediction is substantiated by the infrared studies summarized in Figure 2.

Figure 2 focuses on a region of the infrared spectra most informative for azide compounds. A strong absorption at approximately 2100 cm^{-1} in Figure 2a corresponding to the ν_{N_3} is observed for both submonolayer and multilayer spectra physisorbed at a cryogenic temperature. The shape of this feature does not noticeably depend on coverage. To confirm that this feature represents the azido group, computational studies of a single benzylazide molecule in the gas phase and a benzylazide dimer are also given in Figure 2, in spectra (c) and (d), respectively. The complex structure of the absorption features corresponding to the N3 entity likely depends on the specific interactions among the adsorbed molecules, and the dimer structure is only reported to confirm the fact that these absorption bands split if more than one molecule is taken into account. More importantly, if the submonolayer coverage of benzylazide is briefly annealed to 160 K, in addition to a decrease in intensity of the ν_{N_3} feature, a new absorption band is observed at 2024 cm^{-1} as illustrated in Figure 2b. The absorption features corresponding to any other surface structure with an alternative rearrangement of the N_3 entity (including 1,3-cycloaddition) lie in a different region of the infrared spectrum. Further annealing of the surface giving spectrum (b) in Figure 2 leads to the disappearance of all of the absorption features in the 1900−2300 cm^{-1} region. As evidenced by comparing spectra (b) and (f) in Figure 2, the spectrum of a surface intermediate trapped on a Si(100)-2 × 1 surface after adsorption at 100 K and brief annealing to 160 K can only be explained by the presence of a strongly chemisorbed structure Int2 presented in Figure 1. In this case, the absorption at 2024 cm^{-1} corresponds to a vibration of N_2, whose presence on a surface is stabilized by a neighboring $NCH_2C_6H_5$ group. It should be emphasized that the vibrational spectrum of the 1,3-cycloadduct contains no absorption features in the 1900−2300 cm^{-1} spectral region and thus can be ruled out as the surface species giving rise to the experimentally observed 2024 cm^{-1} peak. It is possible that a reaction pathway similar to that suggested for methylazide can also be predicted for benzylazide; however, the experimental evidence suggests that it is the intermediate Int2 that is observed in the vibrational spectrum presented in Figure 2b.

Thus, we presented direct proof supported by a combination of experimental and computational studies that azido compounds chemisorb on a Si(100)-2 × 1 surface, and this chemisorption is followed by nitrogen elimination, leading to a stable surface adduct based on a Si−Si−N cyclic entity. This chemistry can be further used to introduce a variety of organic groups, especially aromatic substituents, onto a Si(100)-2 × 1 surface.

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Supporting Information Available: References to GridChem and computational methods used, Cartesian coordinates, energies, and predicted vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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