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Competition and Selectivity of Organic Reactions on Semiconductor Surfaces: Reaction of Unsaturated Ketones on Si(100)-2×1 and Ge(100)-2×1

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Abstract: A combined experimental and theoretical study of a model system of multifunctional unsaturated ketones, including ethyl vinyl ketone (EVK), 2-cyclohexen-1-one, and 5-hexen-2-one, on the Si(100)-2×1 and Ge(100)-2×1 surfaces was performed in order to probe the factors controlling the competition and selectivity of organic reactions on clean semiconductor surfaces. Multiple internal reflection infrared spectroscopy data and density functional theory calculations indicate that EVK and 2-cyclohexen-1-one undergo selective [4 + 2] hetero-Diels−Alder and [4 + 2] trans cycloaddition reactions on the Ge(100)-2×1 surface at room temperature. In contrast, on the Si(100)-2×1 surface, evidence is seen for significant ene and possibly [2 + 2] C═O cycloaddition side products. The greater selectivity of these compounds on Ge(100) versus Si(100) is explained by differences between the two surfaces in both thermodynamic factors and kinetic factors. With 5-hexen-2-one, for which [4 + 2] cycloaddition is not possible, a small [2 + 2] C═C cycloaddition product is observed on Ge(100) and possibly Si(100), even though the [2 + 2] C═C transition state is calculated to be the highest barrier reaction by several kilocalories per mole. The results suggest that, due to the high reactivity of clean semiconductor surfaces, thermodynamic selectivity and control will play important roles in their selective functionalization, favoring the use of Ge for selective attachment of multifunctional organics.

I. Introduction

Over the past several years, the clean Si(100)-2×1 and Ge(100)-2×1 surfaces have proved to be remarkable templates for the covalent attachment of organic compounds. These two reactive surfaces share a similar structure consisting of rows of buckled surface dimers which can be described as having both π bond character and zwitterionic diradical character. This dual nature, which allows the Si(100)-2×1 and Ge(100)-2×1 surface dimers to act as both double bonds and electrophilic/nucleophilic moieties, is responsible for the steadily increasing number and types of reactions used to bond organics onto these surfaces over the past several years. The intense interest in studying reactions of organic molecules on semiconductor surfaces arises partly from the potential applications that are expected to result from a marriage of organics and semiconductors in fields such as sensors,[1] molecular electronics,[2] and nanotechnology.[3] To create organic-functionalized semiconductor surface structures with custom-tailored properties, the use of multifunctional compounds and the ability to attach them to the surface in a controlled, selective manner will most likely be required. To achieve this goal, it will be necessary to obtain a greater understanding of how multifunctional compounds, i.e., those with several possible reaction pathways, react with semiconductor surfaces and the factors that control selectivity and competition in these reactions.

Previous work has established that organic molecules can react through one or more C═C double bonds with the Si, Ge, and C(100)-2×1 surfaces to form [2 + 2] cycloaddition and [4 + 2] Diels−Alder adducts.[4−6] For compounds which can react through either pathway (e.g., conjugated dienes), a mixture of products may result, depending on both the molecule and the surface. On the Si(100)-2×1 surface, conjugated dienes have been shown to favor a [4 + 2] Diels−Alder product.[7−9] However, evidence has also shown a minor but significant [2 + 2] product in some cases,[10] even though the Diels−Alder product is thermodynamically favored. This competing side product could be a concern when selective growth of the Diels−

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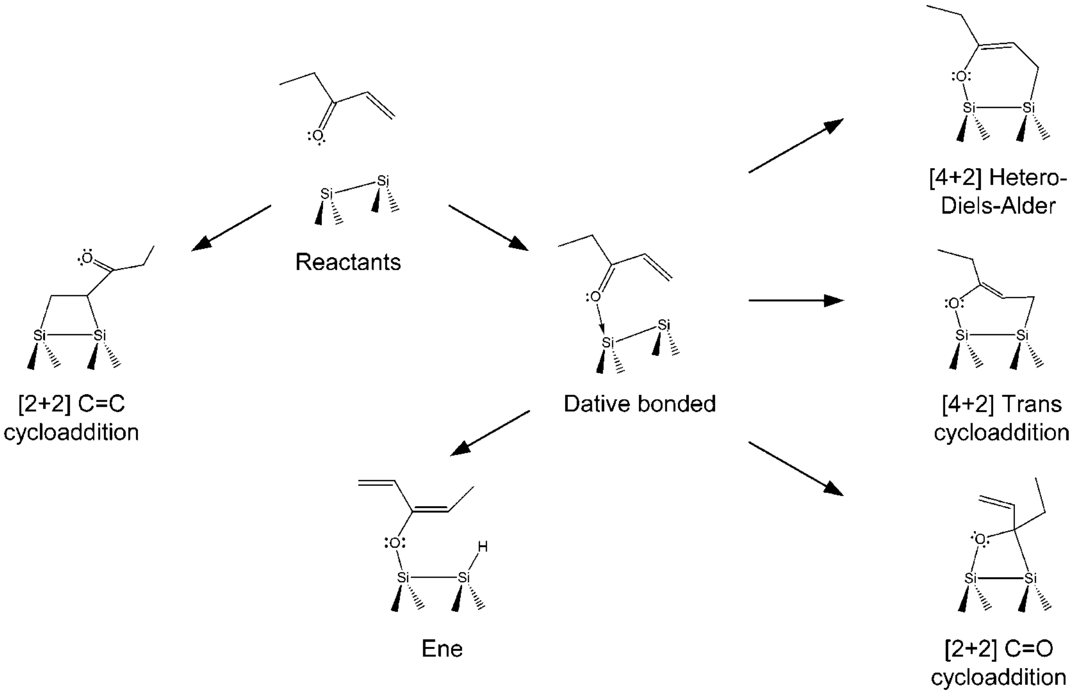

Figure 1. Possible reaction pathways for EVK on Si(100)-2×1 and Ge(100)-2×1.

Alder product is desired. Unfortunately, the use of heat to convert side products to a single thermodynamically favored product (i.e., thermodynamic control) usually results in decomposition due to the strong bonds organics form with silicon. Thus, selectivity is a serious issue for the controlled attachment of organics on clean silicon because the surface is very reactive toward a number of irreversible and kinetically controlled organic reactions. On the Ge(100)-2×1 and C(100)-2×1 surfaces, no evidence has been seen for a competing [2 + 2] reaction for 1,3-butadiene,[11,12] although these studies do not rule out the possibility of its occurrence as a small, unidentified side product.

The carbonyl group is another functionality which can potentially be exploited to attach organics to semiconductor surfaces. White and co-workers found evidence for a [2 + 2] cycloaddition reaction across the C=O bond of simple carbonyl-containing compounds on the Si(100)-2×1 surface.[13,14] On the Ge(100)-2×1 surface, however, we have recently found that acetone does not react to form a [2 + 2] C=O cycloaddition product, even though its formation has the lowest barrier (i.e., it is the kinetic product).[15] Instead, at room temperature acetone undergoes an "ene" reaction in which a thermodynamically favored surface-bound enol-like product is formed via loss of an α-H to the surface.[15] This result was significant in that it demonstrated that thermodynamically controlled organic reactions are possible on semiconductor surfaces, particularly on germanium where reversible desorption is much more likely to occur than on silicon and diamond due to the weaker bonds that are formed with organic molecules. Thermodynamic control is made possible on semiconductor surfaces through high *thermodynamic selectivity*, which we define here in the context of surface reactions as "a measure of the ability to select out adducts based on the reversibility of their weak surface adsorption". Thus, thermodynamic selectivity and control can be exploited as methods for improving selectivity to control attachment on semiconductor surfaces.

In this study, we have investigated the adsorption of ethyl vinyl ketone (EVK) on the Ge(100)-2×1 and Si(100)-2×1 surfaces using multiple internal reflection infrared spectroscopy and density functional theory quantum chemistry calculations. EVK is an α,*β*-unsaturated ketone which contains conjugated C=C and C=O double bonds. Despite its simple structure and functionality, EVK can potentially react with the Si(100) and Ge(100) surfaces through several possible reaction pathways, as shown in Figure 1. The alkene and carbonyl bonds expose EVK to possible [2 + 2] cycloaddition reactions across the C=C and C=O double bonds. EVK may also form a dative bond with the surface via donation of the lone-pair charge of its oxygen. Additionally, when EVK assumes an s-cis conformation, it may potentially undergo a [4 + 2] hetero-Diels−Alder reaction with the surface through its conjugated C=C and C=O bonds. Hetero-Diels−Alder reactions of conjugated dicarbonyls on the Si(100)-2×1 surface have been examined theoretically,[16] although a hetero-Diels−Alder reaction of an α,*β*-unsaturated ketone on a semiconductor surface has not been previously examined either theoretically or experimentally. EVK also contains α-hydrogens and thus may be able to undergo an ene reaction via α-C−H dissociation, as observed previously for acetone on Ge(100)-2×1.[15] The number of possible reactions EVK can undergo with the Si(100) and Ge(100) surfaces makes it an excellent model compound for examining the competition between different reaction pathways.

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In this work we also consider a [4 + 2] reaction with the surface in which the conjugated molecule reacts in a trans or s-trans configuration, as shown for EVK in Figure 1. This reaction is prohibited in organic chemistry since it results in an extremely strained six-membered ring. However, we will show in this paper theoretical and experimental evidence that this reaction, which we call a "[4 + 2] trans cycloaddition", is possible on the Si(100)-2×1 and Ge(100)-2×1 surfaces. For EVK, the hetero-Diels−Alder and trans cycloaddition products are likely to be difficult to distinguish spectroscopically, as they are essentially just cis−trans isomers. Hence, we have also investigated the reaction of another α,β-unsaturated ketone, 2-cyclohexen-1-one, on the Si(100) and Ge(100) surfaces. In 2-cyclohexen-1-one, the conjugated C═C and C═O bonds are locked in a trans configuration, thus providing a means for experimentally examining the viability of the [4 + 2] trans cycloaddition reaction without the possibility of a competing hetero-Diels−Alder reaction. Additionally, we have probed the adsorption of a third unsaturated ketone, 5-hexen-2-one, on the Si(100)-2×1 and Ge(100)-2×1 surfaces. Because the C═C and C═O bonds in 5-hexen-2-one are *not* conjugated, its adsorption behavior then allows examination of the competition between the reactions shown in Figure 1 without the interference of either of the [4 + 2] reactions. Together, these three unsaturated ketones comprise a model system for examining the factors and principles that govern the competition and selectivity of organic reactions on the Si(100)-2×1 and Ge(100)-2×1 surfaces.

II. Experimental and Computational Details

The experiments were performed in an ultrahigh vacuum (UHV) chamber which has previously been described in detail.[17] Infrared data were collected in multiple internal reflection (MIR) mode using a Fourier transform infrared (FTIR) spectrometer with a narrow-band HgCdTe detector. For each experiment, a background IR emissivity spectrum for the clean sample was recorded, and subsequent scans after adsorption were ratioed to this background spectrum and transformed to absorption spectra. For annealing experiments, spectra were taken after the surface had returned to room temperature. Spectra have been corrected for baseline instabilities. The samples, Ge(100) and Si(100) crystals of trapezoidal geometry (1 × 20 × 50 mm, 45° beveled edges), were conductively heated by a resistive tungsten heater and cooled by heat exchange with a liquid nitrogen coldfinger. The sample surfaces were cleaned by sputtering with Ar^+ ions at room temperature followed by annealing to 875 K for 4 min for Ge(100) and 1050 K for ~1 min for Si(100). The quality of the surfaces was verified by sharp monohydride peaks following exposure to atomic hydrogen corresponding with the literature values.[18−20] Additionally, surfaces prepared by the same methods in a different UHV chamber in our laboratory exhibit sharp 2 × 1 LEED patterns. The back faces of the crystals, which are not cleaned by sputtering, were covered with a thin molybdenum plate to prevent adsorption. Ethyl vinyl ketone (98% purity), 2-cyclohexen-1-one (97% purity, Fisher), and 1-hexen-5-one (99% purity, Aldrich) were transferred to sample vials in a nitrogen-purged glovebag and further purified by repeated freeze−pump−thaw cycles before introduction into the chamber through a variable leak valve. All exposures were performed by filling the chamber with the compound for a given pressure and time and are reported in units of Langmuir ($1\ \mathrm{L} = 1 \times 10^{-6}$ Torr·s). The pressures have not been corrected for ion gauge sensitivity.

All calculations in this work were done using the B3LYP hybrid density functional theory (DFT) method with the Gaussian 98 software package.[21] B3LYP has been used extensively to calculate binding and activation energies of organic reactions on Group IV (100)-2×1 surfaces using the cluster approximation. Binding energies calculated using this method are generally in good agreement with experimental results, when available.[22] Additionally, B3LYP has been used to correctly predict that the [4 + 2] reaction of dienes on Si(100)-2×1,[23,24] Ge(100)-2×1,[25] and C(100)-2×1[26] is kinetically and thermodynamically favored over the [2 + 2] reaction, and that *N*-methyl dissociation for amines on Si(100)-2×1 has a prohibitive barrier to dissociation at room temperature while N−H dissociation does not.[22,27] The geometries of all minima and transition states in the potential energy surfaces in this work were calculated at the B3LYP/6-31G(d) level of theory without application of geometry constraints. Geometry optimization was followed by a single-point energy calculation at the more rigorous B3LYP/6-311+G(2df,pd) level of theory, since energies are typically more sensitive to basis set size than geometries. All calculated transition states on the potential energy surfaces were verified by frequency calculations to have one and only one imaginary frequency. The energies reported have not been zero-point corrected.

The Si(100)-2×1 surface is modeled by a Si_9H_{12} one-dimer cluster consisting of four layers of silicon atoms, with the two Si atoms in the top layer comprising the surface dimer. The 7 subsurface Si atoms are terminated with 12 hydrogen atoms to maintain the sp^3 hybridization of the bulk Si atoms. We note that for dative bonding, one-dimer cluster models may not adequately capture charge-transfer effects at the surface.[28] To explore interdimer surface reactions, a $Si_{15}H_{16}$ two-dimer cluster model was employed. To model the Ge(100)-2×1 surface, the top two Si atoms of the Si one-dimer cluster were replaced with Ge atoms ($Ge_2Si_7H_{12}$). A full nine-atom Ge cluster was not used due to the computational expense required. Previous calculations of the [4 + 2] and [2 + 2] cycloaddition reactions of 1,3-butadiene on Ge(100)-2×1 using B3LYP have found that using a $Ge_2Si_7H_{12}$ cluster to model the Ge surface rather than the full Ge_9H_{12} cluster results in less than a 2 kcal/mol difference in the calculated binding energies (which are weaker on $Ge_2Si_7H_{12}$).[25,29] Hence, we expect this approach to be acceptable for modeling the present system.

III. Theoretical Results

To gain a better understanding of the factors controlling competition between organic reactions at semiconductor surfaces, we have calculated the critical points on the potential energy surfaces of the six reactions of EVK shown in Figure 1 for both the Si(100)-2×1 and Ge(100)-2×1 surfaces. Because of their shared structures and similar electronic character, both the Ge(100)-2×1 and Si(100)-2×1 surfaces may undergo the

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same reactions through analogous mechanisms. However, the thermodynamics and kinetics of a particular reaction may vary considerably on the two surfaces, and we will show examples of how this can lead to significant differences in adsorption behavior on Si(100)-2×1 and Ge(100)-2×1. In this section, we present and discuss the calculated thermodynamics of the surface products as well as the kinetics for each of the EVK reaction pathways on the Si(100)-2×1 and Ge(100)-2×1 surfaces.

When considering the theoretical results, it is important to note that the calculation of an energetically favorable reaction product does not ensure that the product will be observed experimentally. The reaction barrier must be accessible, and the binding energy of the reaction product must be sufficient to prevent reversible desorption at the experimental temperature. Additionally, the reaction must compete against all other possible reaction pathways that lead to products which are also stable at the experimental temperature. Unfortunately, activation barriers, particularly small ones, are often difficult to calculate with a high degree of accuracy, and it is possible that a pathway with a lower energy transition state exists. The errors inherent in such computations are exacerbated by the fact that even small differences in activation energies can result in dramatic changes in reaction rate. Dynamical factors which are not calculated and which may differ between reactions will also play important roles in reactivity. For example, for unactivated pathways which lie below the vacuum level, the molecule may not necessarily equilibrate fully in the precursor state and may react directly without a barrier. The facility with which precursor states couple with, and hence lose energy to, the surface will also affect the probability of a given reaction occurring. Proximity to defect sites on the surface could also affect reactivity. Finally, there may be reactions not considered or anticipated that could also compete. Thus, calculated reaction barriers and thermodynamics will be used in conjunction with experimental data rather than to quantitatively predict the product distribution from competing reactions.

We consider first the issue of conformations. We have calculated four stable conformations of molecular EVK due to s-cis and s-trans conformations and rotation of the ethyl group. The calculated energy differences between the gas-phase conformers are negligible, consistent with measurements showing that significant amounts of both s-cis and s-trans conformations exist in equilibrium at room temperature.[30,31] Due to the low calculated cis−trans rotational barrier of 5 kcal/mol for gas-phase EVK, EVK surface adducts are likely to interconvert between conformations on the surface via rotation about single bonds. We have not calculated all the possible conformations for each of the surface reaction products, but for several cases we have found that they may differ in energy by up to a few (0−5) kilocalories per mole. In cases where multiple surface conformations of the same product were calculated, only the lowest-energy product is reported unless otherwise noted.

A. [2 + 2] C=C Cycloaddition. The calculated minima and transition states on the potential energy surfaces of the [2 + 2] cycloaddition reaction of EVK across its C=C bond on both surfaces are shown in Figure 2. We have calculated [2 + 2] C=C adsorption energies of approximately 41 and 28 kcal/mol on the Si(100)-2×1 and Ge(100)-2×1 surfaces, respectively. The smaller binding energy on the Ge(100) surface is due to the weaker strength of Ge−C bonds compared to the strength of Si−C bonds. From these calculations and a previous theoretical study,[25] we estimate that a surface Ge−C bond is approximately 7 kcal/mol weaker than a surface Si−C bond. These [2 + 2] binding energies of EVK are similar to those previously calculated or estimated experimentally for [2 + 2] reactions of alkenes on Si(100) and Ge(100).[9,23−25,32]

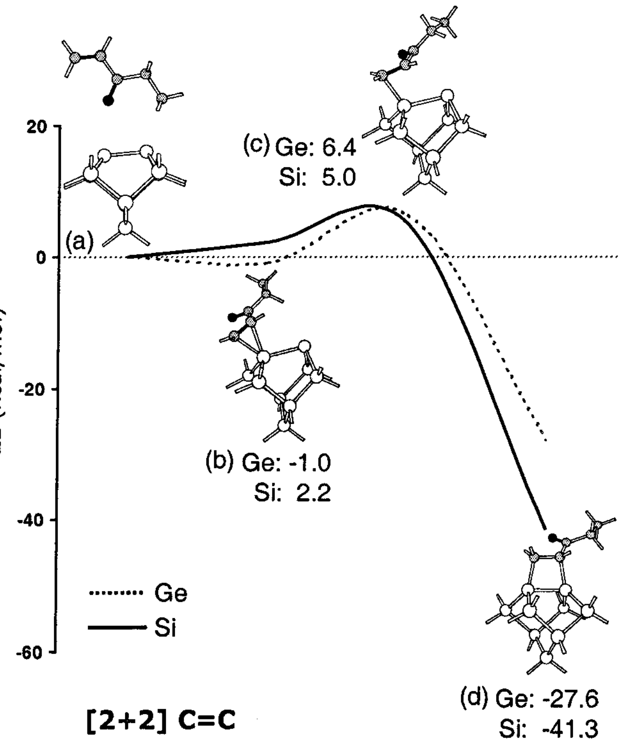

Figure 2. Critical points on the potential energy surfaces of the [2 + 2] C=C cycloaddition reaction of EVK on Si(100)-2×1 and Ge(100)-2×1. Structures shown are optimized on Si(100). The white, black, and gray atoms represent Si, O, and C, respectively. Double bonds are filled in black.

We have located transition states for the [2 + 2] C=C reaction of EVK on both Si(100)-2×1 and Ge(100)-2×1. The optimized geometry and energy of the [2 + 2] C=C transition state on Si(100)-2×1 (Figure 2c), calculated to be 5 kcal/mol above the vacuum level, are similar to those of the [2 + 2] transition state calculated in previous theoretical studies of acetylene,[33] 1,3-cyclohexadiene,[24] pyrrole,[34] thiophene, and furan,[35] with calculated energies of 0−8 kcal/mol. To our knowledge, the [2 + 2] C=C transition state on the Ge(100)-2×1 surface, which for EVK has a calculated energy of 6 kcal/mol, has not been previously reported. A weakly bound "π complex" intermediate, as shown in Figure 2b, was located on each surface and is analogous to the structure first reported by Liu and Hoffmann,[33] although Choi and Gordon later proposed that the π complex intermediate is an artifact of using a single-configurational wave function.[24] Although the calculated [2 + 2] C=C transition states lie several kilocalories per mole above the vacuum level, meaning that the adsorption process is activated, the [2 + 2]

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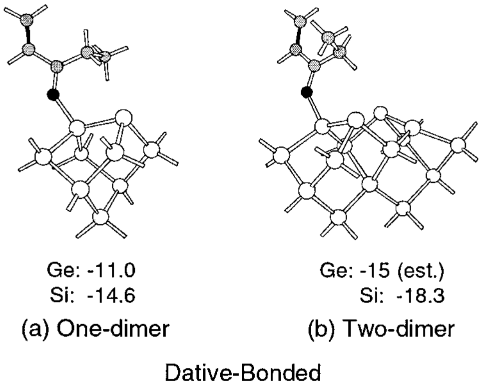

Figure 3. Optimized structures and single-point energies of the dative-bonded state of EVK on a (a) one-dimer cluster and (b) two-dimer cluster.

C═C cycloaddition reaction has been experimentally observed for simple alkenes on both Si(100)-2×1 and Ge(100)-2×1 at room temperature.

B. Dative Bond Formation. On both Si(100)-2×1 and Ge(100)-2×1, the surface dimers are known to be tilted rather than symmetric, giving them a zwitterion-like diradical character in which the "down" atom is slightly positive relative to the "up" atom. Thus, while the dimers of the Si(100)-2×1 and Ge(100)-2×1 surfaces are often described as behaving analogously to C═C double bonds in cycloaddition reactions, each dimer also possesses electrophilic and nucleophilic character. Due to the lone pairs on the oxygen atom, EVK may form a dative bond with the surface by donating charge from the lone pair to the electrophilic "down" atom of a surface dimer, as shown in Figure 1. Previous work has established that amines can form stable dative-bonded structures on the Si(100)-2×1[22,27,36] and Ge(100)-2×1[29] surfaces through the nitrogen lone pair at temperatures as high as room temperature. While acetone forms a stable dative-bonded state at low temperature (115 K) on Ge(100), theoretical and experimental work indicates that surface dative-bonded structures formed via an oxygen lone pair are too weak to persist at room temperature,[15] as opposed to those formed with a nitrogen lone pair.

For the dative-bonded state of EVK on Si(100)-2×1 and Ge(100)-2×1, we have calculated binding energies using a one-dimer cluster of 15 and 11 kcal/mol, respectively, as noted in Figure 3a. These adsorption energies are comparable to those previously calculated for acetone and tetrahydrofuran, and hence the dative-bonded state of EVK is also likely to be observable only at low temperatures (i.e., below room temperature).[15] The dative-bonded state was also calculated on a two-dimer Si(100)-2×1 cluster, as shown in Figure 3b, and was found to have a slightly larger binding energy of ~18 kcal/mol. This stabilization is likely the result of charge transfer from the dative-bonded state to adjacent empty dimer sites and has been studied theoretically for the reaction of ammonia on Si(100)-2×1.[28] Although the computation has not been performed, it is possible that this so-called charge-transfer effect will be even larger on a three-dimer Si(100)-2×1 cluster with two empty sites adjacent to EVK dative bonded in the center dimer. Thus, due to charge-transfer effects, the binding energy of the dative-bonded state will likely depend on whether its adjacent dimer sites (along the same dimer row) are occupied, as delocalization of the charge from the lone pair cannot occur.

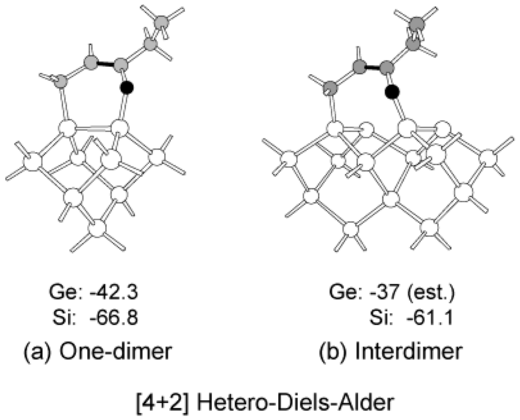

Figure 4. Optimized structures and single-point energies of the (a) one-dimer and (b) interdimer [4 + 2] hetero-Diels−Alder reaction products of EVK.

In addition to being a possible reaction product, the dative-bonded state has significance as a precursor in the [4 + 2] cycloaddition, [2 + 2] C═O cycloaddition, and ene reactions, as shown in Figure 1. Our calculations indicate that formation of the dative bond occurs directly without any activation barrier. It is noted that the calculated EVK dative-bonded structure has its conjugated C═C and C═O bonds in an s-trans conformation. No optimized dative-bonded state could be located for EVK in the s-cis conformation. Instead, we found in our calculations that dative-bonded EVK in the s-cis conformation proceeded directly to a [4 + 2] hetero-Diels−Alder product without a barrier.

C. [4 + 2] Hetero-Diels−Alder Reaction. The [4 + 2] hetero-Diels−Alder reaction of a conjugated dicarbonyl has been previously examined theoretically on the Si(100)-2×1 surface.[16] Here we examine the hetero-Diels−Alder reaction of an α,*β*-unsaturated ketone, EVK, on both Si(100)-2×1 and Ge(100)-2×1. The optimized hetero-Diels−Alder products of EVK on Si(100)-2×1 and Ge(100)-2×1 are shown in Figure 4a, with binding energies of 67 and 42 kcal/mol, respectively. As with normal (nonhetero) conjugated dienes, the hetero-Diels−Alder product of EVK is calculated to be significantly more stable than the [2 + 2] C═C cycloaddition product on both surfaces because there is less ring strain.

For the conjugated dicarbonyl, glyoxal, Barriocanal and Doren have previously calculated a direct, barrierless pathway leading to the hetero-Diels−Alder adduct. This pathway involves stepwise attachment of the carbonyl oxygens to the Si dimer atoms.[16] We have also located a direct, barrierless pathway for the hetero-Diels−Alder reaction of EVK on Si(100)-2×1 and Ge(100)-2×1 that proceeds through dative bond attachment of EVK to the electrophilic "down" atom of a surface dimer followed by attack of the nucleophilic "up" atom by the C═C double bond. Even though we have calculated an energy-minimized dative-bonded state for EVK in the s-trans conformation, there is probably a negligible rotational barrier for conversion to the dative-bonded s-cis conformation, which can proceed without a barrier to form the hetero-Diels−Alder product. Hence, theory indicates that the hetero-Diels−Alder reaction of EVK should proceed with negligible (from the s-trans conformation) or no (from the s-cis conformation) activation barrier on the Si(100)-2×1 and Ge(100)-2×1 surfaces.

The distance between adjacent dimers in the same dimer row (3.84 Å on Si and 4.00 Å on Ge) is small enough that an

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interdimer Diels−Alder reaction across two adjacent dimers (rather than across a single dimer) may be possible. To investigate this possibility, the interdimer hetero-Diels−Alder product of EVK on a two-dimer Si(100)-2×1 cluster was calculated and is shown in Figure 4b. Note that the interdimer reaction results in a seven-membered ring rather than a six-membered ring. With a binding energy of 61 kcal/mol, the hetero-Diels−Alder reaction is only ∼6 kcal/mol less stable across two adjacent dimers than across a single dimer. Moreover, we have calculated a direct, barrierless pathway for the interdimer Diels−Alder reaction of EVK which proceeds through a dative-bonded intermediate analogously to the reaction across a single dimer. Hence, the theory suggests that the interdimer hetero-Diels−Alder reaction may compete with the one-dimer reaction. A likely reason the interdimer reaction is less energetically favorable than the single-dimer reaction is that two dimer π bonds need to be broken rather than one. The strength of the π bonds resulting from the weak overlap of the surface dimer dangling bonds has been estimated to be approximately 2−8 kcal/mol on Si(100)-2×1 and Ge(100)-2×1.[25,37−40] Due to the computational expense involved, the interdimer hetero-Diels−Alder calculation was not repeated on a two-dimer Ge(100)-2×1 cluster. However, we expect this reaction will also proceed directly without a barrier and estimate the adsorption energy to be roughly 37 kcal/mol on the basis of the Si(100)-2×1 results.

D. [4 + 2] Trans Cycloaddition. The [4 + 2] trans cycloaddition reaction has not, to our knowledge, been previously observed on a surface or in organic chemistry due to strain in the resulting trans cyclic product. To investigate the viability of this reaction on semiconductor surfaces, we have calculated the minima and transition states of the potential energy surfaces for the [4 + 2] trans cycloaddition reaction of EVK on Si(100)-2×1 and Ge(100)-2×1, which are shown in Figure 5. The trans cycloaddition products have calculated binding energies of 35 and 14 kcal/mol on the Si(100)-2×1 and Ge(100)-2×1 surfaces, respectively, as shown in Figure 6a. Comparison with the one-dimer [4 + 2] hetero-Diels−Alder surface adducts indicates that the relative strain penalty associated with the trans configuration of the trans cyclic products is approximately 32 kcal/mol on Si(100) and 28 kcal/mol on Ge(100). Although this is a significant amount of strain, the trans product is still thermodynamically favorable on both surfaces. In contrast, we have calculated that the [4 + 2] trans reaction of EVK with ethylene is endothermic by 45 kcal/mol. Thus, while the [4 + 2] reaction of a diene or heterodiene in a trans or s-trans configuration with a C═C double bond is highly improbable, it appears to be at least thermodynamically favorable with the surface dimers of the Si(100)-2×1 and Ge(100)-2×1 surfaces.

Although the thermodynamics for the [4 + 2] trans cycloaddition reaction are favorable for EVK on Si(100)-2×1 and Ge(100)-2×1, it might be expected that the reaction barriers would be prohibitively high due to strain in the transition states. We have calculated transition states for the trans cycloaddition reaction, however, that are approximately 8 and 1 kcal/mol *below* the vacuum level on the Si(100)-2×1 and Ge(100)-2×1 surfaces, respectively (Figure 5c). Thus, the trans cycloaddition reaction of EVK is actually calculated to be an unactivated process on both surfaces. As seen in Figure 5b, the trans cycloaddition reaction proceeds through an s-trans dative-bonded precursor state.

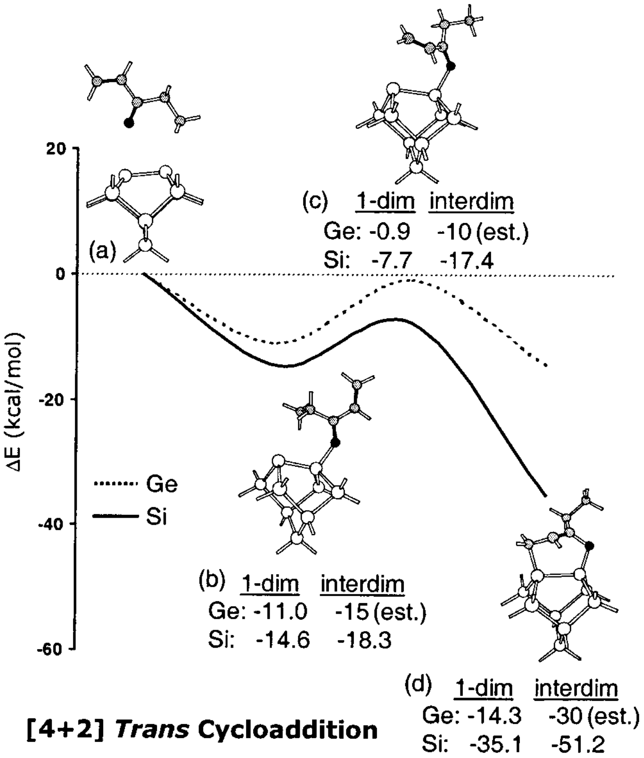

Figure 5. Critical points on the potential energy surfaces of the [4 + 2] trans cycloaddition reaction of EVK on Si(100)-2×1 and Ge(100)-2×1.

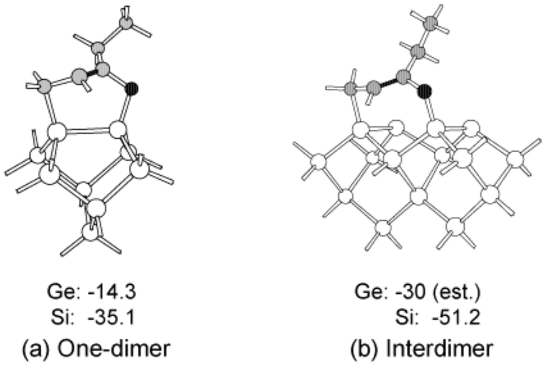

Figure 6. Optimized structures and single-point energies of the (a) one-dimer and (b) interdimer [4 + 2] trans cycloaddition reaction products of EVK.

The interdimer [4 + 2] trans cycloaddition reaction of EVK across adjacent silicon dimers in the same dimer row has also been examined theoretically. The binding energy of the interdimer trans cycloaddition product of EVK on Si(100)-2×1, shown in Figure 6b, was calculated to be 51 kcal/mol and is lower in energy than the one-dimer product by a substantial 16 kcal/mol, despite the cost of the additional silicon dimer π bond that is broken. In fact, the interdimer trans cycloaddition product is only ∼10 kcal/mol less stable than its cis isomer, the interdimer hetero-Diels−Alder product. The large separation of the reacting Si atoms in adjacent dimers (3.8 Å) relative to those

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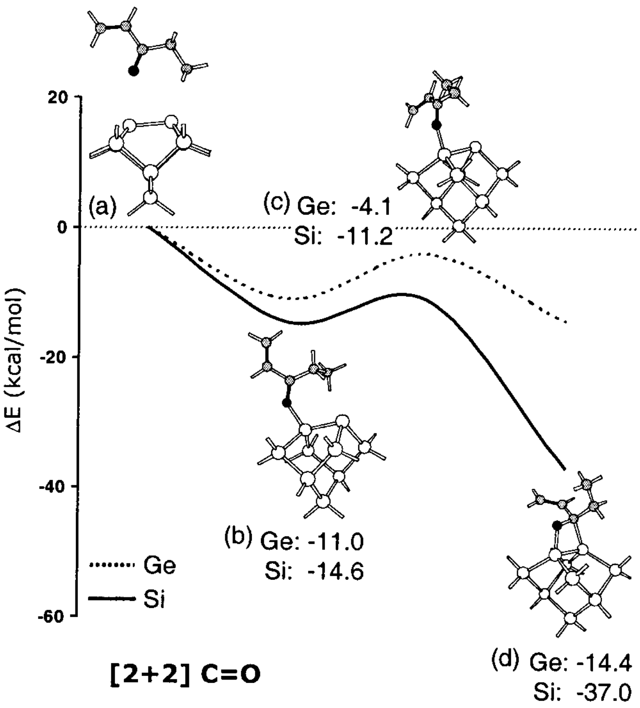

Figure 7. Critical points on the potential energy surfaces of the [2 + 2] C═O cycloaddition reaction of EVK on Si(100)-2×1 and Ge(100)-2×1.

in the same dimer (2.3 Å), in addition to the fact that a seven-membered ring rather than a six-membered ring is formed, allows much of the strain to be relieved in the interdimer versus the one-dimer trans conjugate product. The barrier of the [4 + 2] trans cycloaddition reaction across two adjacent surface dimers is also substantially lower than that across a single dimer, with a calculated transition state 17 kcal/mol below the vacuum level on Si(100)-2×1. The interdimer [4 + 2] trans cycloaddition reaction should also be quite accessible on the Ge(100)-2×1 surface, with an estimated transition-state energy of roughly −11 kcal/mol. Thus, both the kinetics and the thermodynamics of the interdimer [4 + 2] trans cycloaddition reaction across adjacent dimers are significantly favored over those of the intradimer reaction on a single dimer.

E. [2 + 2] C═O Cycloaddition. The [2 + 2] cycloaddition reaction on the Si(100)-2×1 surface of simple ketones and aldehydes across the carbonyl bond to form oxetane-like cycloadducts has been previously reported by Armstrong et al.[13,14] The calculated critical points on the potential energy surfaces for the [2 + 2] C═O cycloaddition reaction of EVK on Si(100)-2×1 and Ge(100)-2×1 are shown in Figure 7. The energy-minimized [2 + 2] C═O cycloaddition products of EVK on Si(100)-2×1 and Ge(100)-2×1 (Figure 7d) have calculated adsorption energies of −37 and −14 kcal/mol, respectively. The weak binding energy of the [2 + 2] C═O addition product on Ge(100)-2×1 is due largely to the surface Ge−O bond strength, which we estimate to be 14−17 kcal/mol weaker than a surface Si−O bond on the basis of the theoretical results. This calculated adsorption energy is insufficient for the [2 + 2] C═O cycloaddition product to persist on Ge(100)-2×1 at room temperature long enough for its observation, as we have shown previously with acetone on Ge(100)-2×1.[15] However, at sufficiently low temperatures, its mean surface residence time will be long enough for the product to be experimentally observed on Ge(100)-2×1 if it is kinetically competitive with the other reaction pathways available to EVK. On the Si(100)-2×1 surface, the binding energy of the [2 + 2] C═O addition product is sufficient for it to remain stably adsorbed at room temperature.

For the [2 + 2] C═O cycloaddition reaction of EVK, transition states (Figure 7c) connecting the *trans*-EVK dative-bonded state to the [2 + 2] C═O addition product were located and had calculated energies of −11 and −4 kcal/mol on the Si(100)-2×1 and Ge(100)-2×1 surfaces, respectively. Thus, like acetone but unlike formaldehyde and glyoxal, which were previously calculated to have barrierless [2 + 2] C═O addition pathways,[16,41] the theory suggests that the [2 + 2] C═O addition reaction of EVK on Si(100) and Ge(100) must pass through a transition state which lies above a dative-bonded precursor state in energy. Since all points on the reaction pathway lie below the reactants, the [2 + 2] C═O cycloaddition reaction is unactivated on both surfaces. However, we previously found that acetone lacks sufficient energy to undergo [2 + 2] C═O cycloaddition at 115 K, even though the overall reaction was also calculated to be unactivated, and instead is trapped in its dative-bonded precursor state.[15] Those results suggest that, for EVK, the relative transition-state energies for even the unactivated reactions will play a critical role in the competition between reactions.

F. Ene Reaction. The ene reaction, which involves the loss of an α-H, was observed experimentally on a semiconductor surface for the room-temperature reaction of acetone on Ge(100)-2×1.[15] Because EVK also contains α-hydrogens, it also might undergo an ene reaction with the Si(100)-2×1 and Ge(100)-2×1 surfaces, as shown in Figure 1. In this reaction, EVK can be considered the “ene” and the Si(100)-2×1 or Ge(100)-2×1 surface dimer the “enophile”. Note that the ene reaction of a ketone on the Si(100)-2×1 or Ge(100)-2×1 surface results in an enol-like product, and hence it may also be considered an enolization reaction.

The critical points on the potential energy surfaces for the ene reaction of EVK on Si(100)-2×1 and Ge(100)-2×1 are shown in Figure 8. The ene binding energies of approximately 46 and 23 kcal/mol on the Si(100)-2×1 and Ge(100)-2×1 surfaces, respectively (Figure 8d), are comparable to those calculated for the ene reaction of acetone.[15] Unlike the [2 + 2] C═O cycloaddition reaction product on Ge(100)-2×1, the more thermodynamically favorable ene adduct of EVK on Ge(100)-2×1 is calculated to be stable at room temperature (using a first-order Arrhenius expression and a typical pre-exponential factor of 10^{13} s^{-1}), and indeed the ene adduct of acetone on Ge(100)-2×1 has been previously observed at room temperature.[15]

A transition state (Figure 8c) connecting the stable *trans*-EVK dative-bonded precursor state to the ene product on both surfaces was found to lie approximately 13 kcal/mol below the vacuum level on Si(100)-2×1 and at the vacuum level on Ge(100)-2×1. These barriers are surprisingly low for a reaction involving C−H dissociation, which may be due in part to the high acidity of α hydrogens in ketones and aldehydes. We previously proposed that the resonance stabilization responsible for the high acidity of the α hydrogens could also take place in the transition state for the ene reaction on Si(100)-2×1 and Ge(100)-2×1, resulting in a low barrier.[15] The correlation between ease of C−H cleavage at the surface and high acidity

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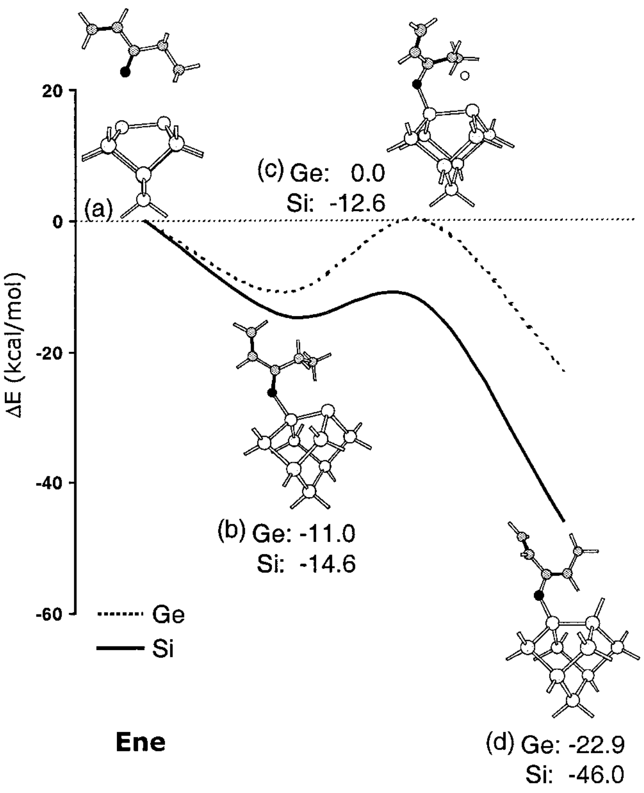


Figure 8. Critical points on the potential energy surfaces of the ene reaction of EVK on Si(100)-2×1 and Ge(100)-2×1.

indicates a mechanism of proton transfer to the nucleophilic "up" atom of the surface dimer from the dative-bonded precursor state rather than homolytic bond cleavage.

IV. Ethyl Vinyl Ketone Experimental Results

A. EVK Adsorption on Ge(100)-2×1. We begin our examination of the experimental results with the reaction of EVK on the Ge(100)-2×1 surface. Figure 9b shows the Ge(100)-2×1 surface following a saturation dose (100 L) of EVK at room temperature. Notable in the room-temperature IR spectrum is the absence of the intense peaks associated with the carbonyl stretching mode of EVK, which can be seen in the physisorbed multilayer spectrum of molecular EVK at ~1675 and 1700 cm^{-1} (Figure 9c). This result is important as it rules out a [2 + 2] C═C cycloaddition product (Figure 2d), which would still have its carbonyl bond intact. No significant ν(Ge−H) stretch can be seen in the 1900−2000 cm^{-1} region of the IR spectrum of EVK on Ge(100) as well. This precludes the possibility of a significant ene product, as ν(Ge−H) as well as ν(Si−H) surface modes are both known to be intense.[17,20] Additionally, due to thermodynamics, both the dative-bonded and [2 + 2] C═O cycloaddition adducts can be ruled out at room temperature on the basis of their calculated binding energies. The remaining alkene stretch at 1620 cm^{-1}, the sp^2 ν(C−H) mode at ~3033 cm^{-1}, and the apparent loss of the asymmetric vinylic CH_2 stretch at 3097 cm^{-1} in Figure 9b are all consistent with the formation of [4 + 2] products. *Thus, the data indicate that EVK undergoes [4 + 2] cycloaddition at room temperature on Ge(100)-2×1.*

Because the [4 + 2] hetero-Diels−Alder (Figure 4) and [4 + 2] trans cycloaddition (Figure 6) products are essentially cis−trans isomers, these will be spectroscopically similar and consequently difficult to distinguish. Although the [4 + 2] hetero-Diels−Alder reaction is calculated to be kinetically favored over the [4 + 2] trans cycloaddition reaction, the interdimer trans cycloaddition reaction has only a minor barrier and hence may compete kinetically. Thus, an interdimer trans cycloaddition side product (Figure 6b) cannot be ruled out on the basis of the spectroscopic results. However, the *one-dimer* trans cycloaddition product (Figure 6a), with a binding energy of only ~14 kcal/mol, is calculated to be unstable on Ge(100)-2×1 at room temperature, and thus it can be ruled out.

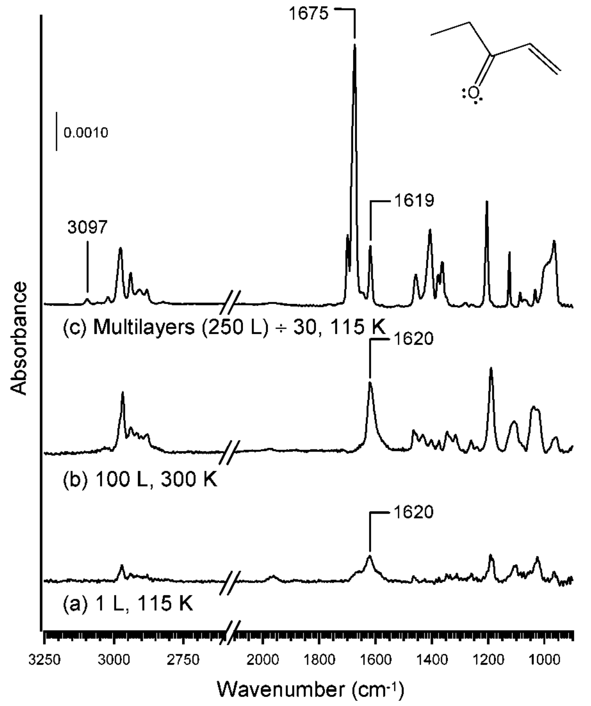


Figure 9. Infrared spectra of EVK on the Ge(100)-2×1 surface: (a) 1 L at 115 K; (b) 100 L at 300 K; (c) multilayers (scaled) at 115 K.

While some interdimer trans cycloaddition product might be formed initially upon adsorption of EVK on Ge(100)-2×1, conversion to the hetero-Diels−Alder product may occur. Direct conversion of the trans cycloaddition product (the trans isomer) to the hetero-Diels−Alder product (the cis isomer) via rotation about the carbon−carbon double bond is improbable due to the high cost of breaking the π bond (~63 kcal/mol). However, the barrier for conversion of the interdimer trans cycloaddition reaction to the trans dative-bonded precursor state (i.e., Ge−C bond cleavage) on Ge(100)-2×1 is estimated to be only 20 kcal/mol. The trans dative-bonded product can then convert to its s-cis conformation with a minimal (~5 kcal/mol) barrier, which can proceed directly to the hetero-Diels−Alder product without barrier. The calculated half-life time for this conversion process at room temperature is only about 3 min using a typical pre-exponential factor of 1×10^{-13} s^{-1} and a first-order Arrhenius expression. Thus, any initial trans cycloaddition product formed may convert to the hetero-Diels−Alder product on the Ge(100) surface on experimental time scales. Because the hetero-Diels−Alder product is substantially more stable than the trans cycloaddition product, its conversion rate back to the trans cycloaddition product is negligible, and thus the equilibrium established will greatly favor the hetero-Diels−Alder product. Whether the hetero-Diels−Alder product exists in its one-dimer or interdimer form (or a mixture of both forms) cannot be determined on the basis of the IR data due to the likely spectroscopic similarity of the two forms. We plan to perform scanning tunneling microscopy studies to determine the relative amounts of one-dimer versus interdimer adducts and whether trans cycloaddition products are present in addition to the hetero-Diels−Alder products.

At sufficiently low temperatures, the dative-bonded and [2 + 2] C═O reaction products should remain stable on the surface, allowing them to be observed. In addition, there may be insufficient energy at low temperature to overcome reaction barriers which are accessible at room temperature, resulting in a change in product distribution. To investigate these possibilities, the reaction of EVK on Ge(100)-2×1 was examined at 115 K. Figure 9a shows an infrared spectrum of the Ge(100)-2×1 surface after exposure to 1 L of EVK at 115 K. The low-temperature spectrum in Figure 9a is virtually identical in shape to the room-temperature spectrum in Figure 9b, indicating the presence of the hetero-Diels−Alder product at low temperature. The shoulder seen at ∼1670 cm^{-1} in Figure 9a is attributed to the intense carbonyl stretching mode of a small amount of physisorbed EVK, which continues to grow in at higher exposures (not shown) of EVK at 115 K along with more of the hetero-Diels−Alder product. The position of the carbonyl stretch, which is close to that of the physisorbed spectrum in Figure 9c, indicates that it is not attributable to dative-bonded EVK since previous experiments[15] indicate that the carbonyl stretch is significantly shifted downward in frequency upon dative bonding. The lack of additional modes at 115 K indicates that the [2 + 2] C═O reaction does not compete kinetically with the [4 + 2] reaction or is inaccessible at low temperatures on Ge(100)-2×1. A weak ν(Ge−H) peak is seen at ∼1960 cm^{-1}, which along with a ν(O−H) peak at ∼3630 cm^{-1} (not shown) is attributed to a small amount of dissociative water adsorption.

The fact that the hetero-Diels−Alder reaction proceeds at low temperature (115 K) supports the calculations, which predict a negligible barrier for the hetero-Diels−Alder reaction. Although the dative-bonded state has no barrier and is formed with sufficient binding energy to remain stable at 115 K, it is a precursor to the [4 + 2] hetero-Diels−Alder reaction and hence is not observed as a stable, isolatable state for EVK. In contrast, with acetone, which does not possess the conjugation system necessary to undergo a [4 + 2] reaction, the dative-bonded state *is* observed on Ge(100)-2×1 at 115 K.[15] The ene and [2 + 2] C═O cycloaddition reactions have relatively small but finite barriers with transition states very near to the vacuum level on Ge(100)-2×1. These reactions are either energetically inaccessible at 115 K or cannot compete kinetically with the barrierless [4 + 2] hetero-Diels−Alder reaction. These studies indicate that significant energy is lost in the dative-bonded precursor state, possibly through phonon coupling with the semiconductor, which reduces the energy available to surmount reaction barriers and causes some unactivated pathways to be kinetically inaccessible at low temperatures.

To probe the thermal stability of the [4 + 2] products, annealing IR studies were performed after a saturation dose of EVK on Ge(100)-2×1 at room temperature. Figure 10 shows the infrared spectra of EVK on Ge(100)-2×1 at room temperature and after successive anneals to 400 and 500 K. It can be seen that annealing to 400 K (Figure 10b) has essentially no effect on the room-temperature adduct. Following a successive anneal at 500 K (Figure 10c), evidence of some decomposition and/or desorption can be seen by the loss in intensity of most modes as well as the growth of a ν(Ge−H) mode at 1965 cm^{-1}.

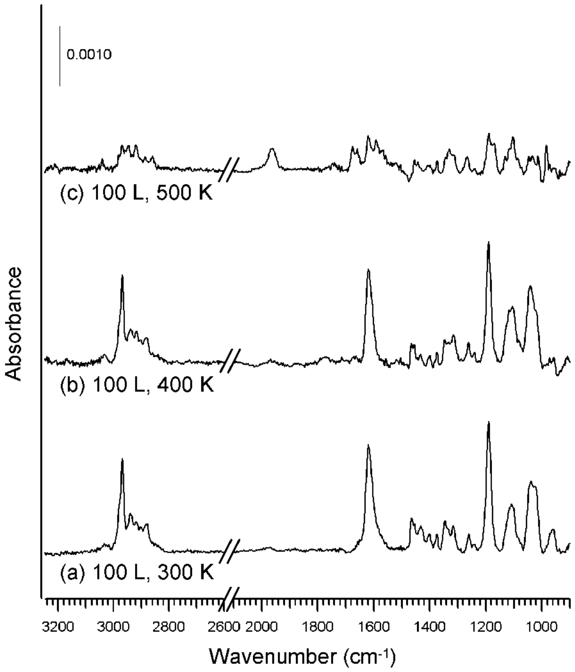


Figure 10. Infrared spectra of an annealing series of EVK on the Ge(100)-2×1 surface: (a) 100 L at 300 K; (b) followed by annealing at 400 K; (c) followed by annealing at 500 K.

B. EVK Adsorption on Si(100)-2×1. Our theoretical calculations indicate that the Si(100)-2×1 surface differs from the Ge(100)-2×1 surface mainly in that on Si(100) the reaction products are substantially more stable and the barriers to adsorption are smaller. Hence, the observed chemistry of EVK may differ on the Si(100)-2×1 surface compared to that on Ge(100)-2×1 due to both thermodynamic and kinetic factors. A saturation exposure of EVK on the Si(100)-2×1 surface at room temperature is shown in Figure 11a. Significant growth of Si−H is evident from the peak at ∼2071 cm^{-1}, indicating α-C−H dissociation from the ene reaction upon adsorption, in contrast to the reaction of EVK on the Ge(100)-2×1 surface, where no significant ene product was observed. We estimate that the ene product occupies roughly one-quarter to one-third of reactive silicon surface dimers. This value is obtained by comparing the integrated intensity of the ν(Si−H) mode to that of a Si(100)-2×1 surface exposed to a saturation dose of water at room temperature, which is known to have one Si−H and one Si−OH bond per surface dimer due to dissociative adsorption.

While the modes below ∼1550 cm^{-1} cannot be seen on the silicon surface due to IR absorption by crystal phonon modes, the C−H stretch region is practically identical in both shape and size to that of EVK on Ge(100)-2×1. This observation, together with the calculation of a barrierless pathway for the [4 + 2] hetero-Diels−Alder reaction on Si(100)-2×1, suggests that [4 + 2] adducts are the major species on the Si(100)-2×1 surface as well. Along with the [4 + 2] hetero-Diels−Alder and ene adducts, the interdimer trans cycloaddition product (Figure 6b) is expected to exist on Si(100)-2×1 since its transition state is ∼5 kcal/mol below that of the observed ene reaction.

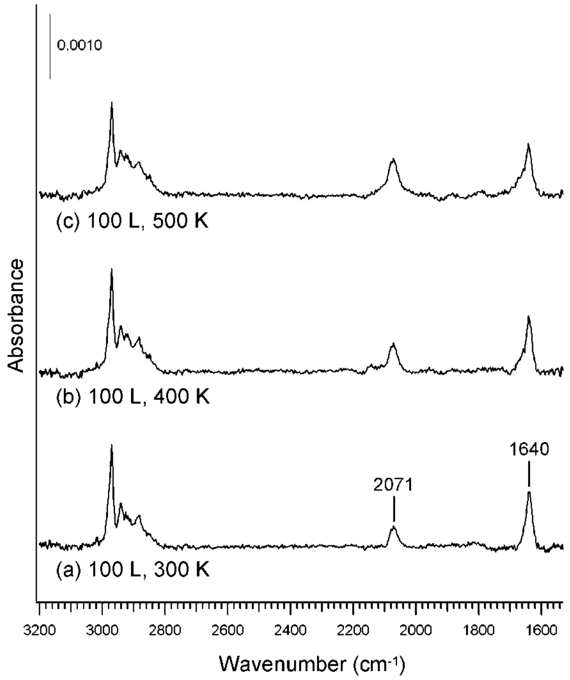


Figure 11. Infrared spectra of an annealing series of EVK on the Si(100)-2×1 surface: (a) 100 L at 300 K; (b) followed by annealing at 400 K; (c) followed by annealing at 500 K.

Additionally, in contrast to Ge(100)-2×1, conversion from the interdimer trans cycloaddition product to the hetero-Diels−Alder product on Si(100)-2×1 is unlikely at room temperature due to a calculated barrier of approximately 34 kcal/mol for this process. It is also possible that the one-dimer trans cycloaddition product and the [2 + 2] C═O cycloaddition product are present, because unlike on Ge(100), for Si(100) they are both calculated to be stable at room temperature. However, quantification of the amount of [2 + 2] C═O and [4 + 2] trans cycloaddition products is difficult, as they likely resemble spectroscopically the hetero-Diels−Alder cycloaddition product in that their formation results in the loss of the carbonyl bond in EVK but leaves an alkene double bond.

Annealing IR studies were performed on the room-temperature adduct of EVK on Si(100)-2×1 and are shown in Figure 11. It can be seen that there is little change in the IR spectrum following anneals at 400 K (Figure 11b) and 500 K (Figure 11c), indicating high thermal stability of the room-temperature products. In contrast, significant desorption and/or decomposition had occurred following the 500 K anneal on the Ge(100)-2×1 surface. The high thermal stability observed is consistent with the substantially stronger bonds formed on Si(100)-2×1 versus Ge(100)-2×1. We note that a high binding energy does not ensure that a surface product will remain stable up to its predicted unimolecular desorption temperature, as there may be alternative decomposition or conversion pathways with more favorable kinetics.

V. 2-Cyclohexen-1-one: [4 + 2] Trans Cycloaddition

For EVK, the presence of the interdimer [4 + 2] trans cycloaddition product on Si(100)-2×1 could be inferred from its relative kinetics, but the product could not be directly identified due to its spectroscopic similarity to the cis isomer, the [4 + 2] hetero-Diels−Alder product. To further investigate the [4 + 2] trans cycloaddition reaction, we have studied the adsorption of 2-cyclohexen-1-one on the Ge(100)-2×1 and Si(100)-2×1 surfaces. Because its conjugated C═C and C═O bonds are locked in a trans configuration, 2-cyclohexen-1-one cannot undergo a hetero-Diels−Alder reaction, which requires a cis configuration. Thus, unlike EVK, 2-cyclohexen-1-one provides a means for examining the viability of the [4 + 2] trans cycloaddition reaction without the possibility of interference from the [4 + 2] hetero-Diels−Alder reaction.

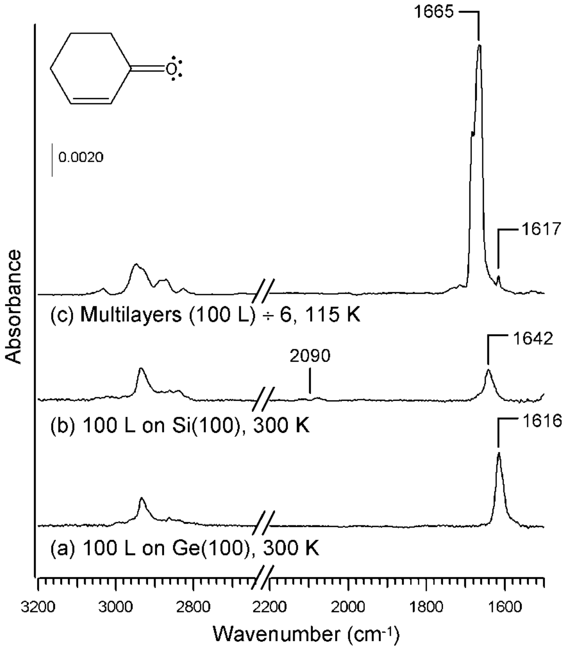
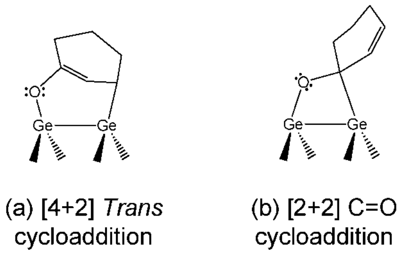


Figure 12. Infrared spectra of 2-cyclohexen-1-one: (a) 100 L on Ge(100)-2×1 at 300 K; (b) 100 L on Si(100)-2×1 at 300 K; (c) multilayers (scaled) at 115 K.

Figure 12a shows the infrared spectrum of a saturation dose (100 L) of 2-cyclohexen-1-one on Ge(100)-2×1 at room temperature. Notable in the spectrum is a strong peak at 1616 cm^{-1}, which we assign to a ν(C═C) mode since a non-dative-bonded ν(C═O) mode is not expected in this region. Because the hetero-Diels−Alder reaction is not possible for 2-cyclohexen-1-one due to the trans configuration of its double bonds and the [2 + 2] C═O product is calculated to be unstable at room temperature, the presence of the alkene mode indicates possible ene or [4 + 2] trans cycloaddition products. However, the ene reaction involves transfer of an α-H to the surface, and only a very small ν(Ge−H) mode can be seen in the spectrum, thus ruling out the ene reaction as a significant pathway. Note that the strength of the alkene stretch is several times larger than its relative intensity in the physisorbed spectrum in Figure 12c at 1617 cm^{-1} and approaches the intensity of a carbonyl band. This phenomenon is known for ethers in which an alkene group is directly connected to the ether oxygen. The trans cycloaddition product does, indeed, have an ether-like oxygen connected to a C═C double bond, whereas the [2 + 2] C═O cycloaddition product does not, as shown in Figure 13. Additionally, the [2 + 2] C═O cycloaddition adduct can be ruled out as a stable product at room temperature on the basis of its energetics. Thus, the data are consistent with a [4 + 2] trans cycloaddition reaction of 2-cyclohexen-1-one to the Ge(100)-2×1 surface. This is significant in that it provides, to the best of our knowledge, the first experimental evidence of cycload-



(a) [4+2] *Trans* cycloaddition (b) [2+2] C=O cycloaddition

Figure 13. Comparison of the (a) [4 + 2] trans cycloaddition and (b) [2 + 2] C=O cycloaddition products of 2-cyclohexen-1-one on Ge(100)-2×1. In (a) the O is adjacent to the C=C bond, while in (b) it is not adjacent.

Table 1. 2-Cyclohexen-1-one Calculations

	Si(100)	Ge(100)
[2 + 2] C=C cycloaddition product	−32.6	−19.4
[4 + 2] trans cycloaddition product	−27.2	−8.0
[4 + 2] trans cycloaddition interdimer product	−42.8	−24[a]
[2 + 2] C=O cycloaddition product	−34.9	−11.9
ene product	−45.6	−23.1

[a] Estimated.

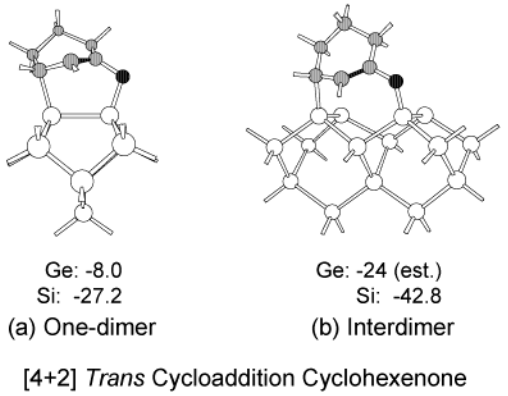


Figure 14. Optimized structures and single-point energies of the (a) one-dimer and (b) interdimer [4 + 2] trans cycloaddition reaction products of 2-cyclohexen-1-one.

dition of a trans diene or heterodiene either with another molecule or at a surface.

Theoretical calculations for 2-cyclohexen-1-one, shown in Table 1, indicate that the [4 + 2] trans cycloaddition reaction across a single Ge dimer is too strained to persist at room temperature, with a binding energy of only 8 kcal/mol. However, when the reaction occurs across two adjacent dimers in the same row, as shown in Figure 14, the ring strain is diminished and the binding energy is significantly increased to an estimated 24 kcal/mol, a value sufficient for room-temperature stability. Thus, the theory suggests that the [4 + 2] trans cycloaddition reaction of 2-cyclohexen-1-one on Ge(100)-2×1 at room temperature occurs across two dimers rather than a single dimer.

The adsorption of 2-cyclohexen-1-one on the Si(100)-2×1 surface has also been investigated. The IR spectrum of a saturation dose (100 L) of 2-cyclohexen-1-one on the Si(100)-2×1 surface at room temperature is shown in Figure 12b. The C−H stretch region is nearly identical to that of 2-cyclohexen-1-one on Ge(100)-2×1 (Figure 12a), suggesting that the [4 + 2] trans cycloaddition adduct is the major species on the Si(100)-2×1 surface as well. The presence of Si−H at ~2090 cm^{-1} indicates a side product from the ene reaction, which we estimate is present on roughly one-quarter of reactive surface dimers on the basis of comparison with a Si−OH- and Si−H-terminated Si(100)-2×1 surface from dissociative chemisorption of water. Thus, as with EVK, the selectivity of 2-cyclohexen-1-one is greater on Ge(100) than on Si(100), with a significant ene side product present on the Si(100)-2×1 surface but absent on the Ge(100)-2×1 surface.

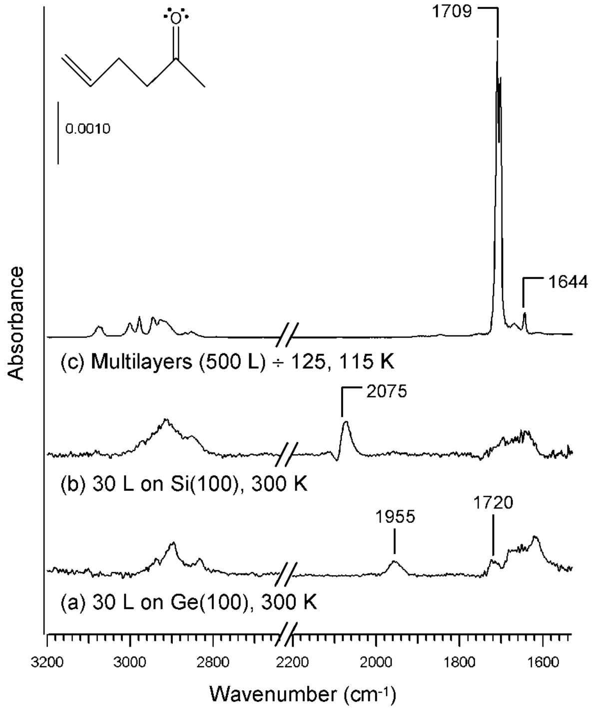


Figure 15. Infrared spectra of 5-hexen-2-one: (a) 30 L on Ge(100)-2×1 at 300 K; (b) 30 L on Si(100)-2×1 at 300 K; (c) multilayers (scaled) at 115 K.

VI. 5-Hexen-2-one: Removal of Conjugation

The EVK and 2-cyclohexen-1-one data show that the [4 + 2] hetero-Diels−Alder and [4 + 2] trans cycloaddition reactions are favored over competing reactions on the Ge(100) surface and, to a lesser extent, on the Si(100) surface. Since it is the conjugation of the C=C and C=O double bonds that makes the [4 + 2] reactions possible, removing this conjugation will allow examination of the competition between the [2 + 2] C=C addition, [2 + 2] C=O addition, and ene reactions without the interference of the kinetically and thermodynamically favored [4 + 2] reactions. To this end, we have investigated with IR spectroscopy the reaction of the nonconjugated 5-hexen-2-one on the Ge(100)-2×1 and Si(100)-2×1 surfaces.

The IR spectrum of a saturation dose (30 L) of 5-hexen-2-one on the Ge(100)-2×1 surface at room temperature is shown in Figure 15a. The presence of a ν(Ge−H) mode at ~1955 cm^{-1} is indicative of an ene adduct, which is significant in that neither EVK nor 2-cyclohexen-1-one formed substantial ene products on Ge(100)-2×1. We estimate that the ene product for 5-hexen-2-one occupies roughly one-quarter of reactive surface dimers on the basis of the integrated intensity of the ν(Ge−H) mode. Another significant observation in the IR data is the presence of a small carbonyl mode at ~1720 cm^{-1}. The carbonyl mode indicates the presence of a [2 + 2] C=C cycloaddition adduct, since it is the only product in which the carbonyl bond remains intact. This mode was not observed for EVK or 2-cyclohexen-1-one on either the Ge(100)-2×1 or Si(100)-2×1 surfaces. Because the intensity of the carbonyl mode is weak relative to its intensity in the physisorbed spectrum of molecular 5-hexen-2-one in Figure 15c, we believe the amount of [2 + 2] C═C cycloaddition product is small. As the [2 + 2] C═O cycloaddition adduct is not expected to be stable at room temperature on the Ge(100)-2×1 surface, accounting for the ene and [2 + 2] C═C addition products suggests that there are a substantial number of unreacted surface dimers at saturation. This claim is supported by the observation that the intensity of the surface modes in Figure 15a is less than those of EVK (Figure 9b) and 2-cyclohexen-1-one (Figure 11a) on Ge(100)-2×1. It may be that steric factors have a limiting effect on the saturation coverage of 5-hexen-2-one, as its reaction products all have a relatively long chain protruding out from the surface dimer.

We have also investigated the adsorption of 5-hexen-2-one on the Si(100)-2×1 surface. Figure 15b shows the IR spectrum of the Si(100)-2×1 surface following a saturation dose (30 L) of 5-hexen-2-one at room temperature. We estimate from the integrated intensity of the ν(Si−H) mode at ~2075 cm^{-1} that the ene product occupies roughly one-half of the surface dimers on Si(100). This is a greater amount of ene product than was observed for saturation coverages of EVK and 2-cyclohexen-1-one on the Si(100)-2×1 surface, which we attribute to the fact that there are no competing [4 + 2] pathways available to 5-hexen-2-one. Interestingly, the coverage of the 5-hexen-2-one ene product on Si(100)-2×1 is approximately twice that on Ge(100)-2×1. It may be possible that the higher binding energies on Si(100)-2×1 relative to Ge(100)-2×1 cause the silicon surface products to be less sensitive to destabilization from crowding and allow a higher coverage to be attained. In addition to the ene product, a minor amount of [2 + 2] C═C cycloaddition product may also be present, although the features in the carbonyl region are less distinct and intense on Si(100)-2×1 than on Ge(100)-2×1. While the [2 + 2] C═O addition reaction is expected to compete with the ene reaction on the Si(100)-2×1 surface at room temperature, we have not quantified the amount of [2 + 2] C═O addition product due to its lack of an identifying spectroscopic feature.

VII. Discussion

A. Competition and Selectivity. Although many reactions of organics on semiconductor surfaces have been reported in the past several years, the principles and factors that control reactivity at these surfaces are still not well understood. From an examination of the combined theoretical and experimental results of this model system of unsaturated ketones, an understanding can be gained not only of the semiconductor surface chemistry of these multifunctional compounds, but also of the factors that govern competition and selectivity of organic reactions on clean semiconductor surfaces in general. Ethyl vinyl ketone and 2-cyclohexen-1-one, both α,β-unsaturated ketones, undergo [4 + 2] cycloaddition reactions on the Si(100)-2×1 and Ge(100)-2×1 surfaces. These [4 + 2] hetero-Diels−Alder cycloaddition and [4 + 2] trans cycloaddition reactions are selective on the Ge(100)-2×1 surface over competing reactions such as the [2 + 2] C═C cycloaddition, [2 + 2] C═O cycloaddition, and ene reactions. On the Si(100)-2×1 surface, the [4 + 2] cycloaddition reactions are also favored over the competing reactions, although to a lesser degree than on the Ge(100)-2×1 surface, as significant side products are observed. *Thus, the results indicate that the chemistry of EVK and 2-cyclohexen-1-one is markedly more selective on the Ge(100)-2×1 surface than on the Si(100)-2×1 surface.*

An examination of the theoretical calculations provides valuable insight into understanding why the [4 + 2] cycloaddition reactions are more selective on the Ge(100)-2×1 surface than on the Si(100)-2×1 surface. Because all the considered reactions except for [2 + 2] C═C cycloaddition share the dative-bonded state as a common intermediate, direct comparisons of their barriers can be made. On both Ge(100)-2×1 and Si(100)-2×1, we have calculated direct, barrierless pathways for the hetero-Diels−Alder reaction of EVK in which the reaction proceeds without traversing through a transition state. In contrast, barriers were calculated for the competing reaction pathways on the Ge(100)-2×1 and Si(100)-2×1 surfaces which are significantly higher in energy on Ge(100)-2×1 than on Si(100)-2×1. Thus, the difference in activation energies between the hetero-Diels−Alder reaction of EVK and the other competing reactions is increased on the Ge(100)-2×1 surface relative to the Si(100)-2×1 surface. *This greater separation in barriers causes an increase in the branching ratio which leads to the enhanced selectivity of the [4 + 2] hetero-Diels−Alder reaction observed on the Ge(100)-2×1 surface relative to the Si(100)-2×1 surface.*

Unlike the [4 + 2] hetero-Diels−Alder reaction, the interdimer [4 + 2] trans cycloaddition reaction, which is the favored reaction for 2-cyclohexen-1-one at room temperature, does have a finite barrier that is calculated to be larger on Ge(100)-2×1 than on Si(100)-2×1. Hence, the explanation given for the enhanced selectivity of the reaction of EVK on Ge(100)-2×1 over Si(100)-2×1 would not seem to apply for 2-cyclohexen-1-one. For example, using the calculated kinetics for EVK, the barrier for the interdimer trans cycloaddition reaction is approximately 5 kcal/mol lower in energy than its closest *kinetic competitor*, the ene reaction, on the Si(100)-2×1 surface. On the Ge(100)-2×1 surface, the trans cycloaddition barrier is approximately 6 kcal/mol lower in energy than the next most kinetically favorable reaction, [2 + 2] C═O cycloaddition. Given the observed competition that occurs for the unsaturated ketones on the Si(100)-2×1 surface for reactions whose barriers are separated by even several kilocalories per mole, this difference of ~1 kcal/mol in barrier separation is not sufficient to explain the improved selectivity observed on Ge(100)-2×1 versus Si(100)-2×1 for 2-cyclohexen-1-one.

To explain the greater selectivity of 2-cyclohexen-1-one on Ge(100)-2×1 versus Si(100)-2×1, it is necessary to consider another factor: thermodynamic selectivity. As previously discussed, the [2 + 2] C═O cycloaddition product is not stable on Ge(100)-2×1 at room temperature due to its weak binding energy. This means that the closest kinetically *and thermodynamically* viable competitor to the interdimer trans cycloaddition reaction on Ge(100)-2×1 is the ene reaction, not the [2 + 2] C═O cycloaddition reaction. The barrier difference on Ge(100) between the interdimer trans cycloaddition reaction and the ene reaction is around 10 kcal/mol. This increased difference between reaction barriers on Ge(100), due to thermodynamic selectivity, compared to Si(100) is probably sufficient to account for the improved selectivity of the interdimer trans cycloaddition reaction of 2-cyclohexen-1-one on Ge(100) versus Si(100). Thus, it is necessary to consider *thermodynamic factors (i.e., improved thermodynamic selectivity) in addition to kinetic factors* in order to explain why the chemistry of 2-cyclohexen-1-one is selective on Ge(100)-2×1 but not on Si(100)-2×1.

Although Si(100)-2×1 and Ge(100)-2×1 surfaces share a common structure and react with organics through analogous mechanisms, we observed that the chemistry on these surfaces is significantly different. These differences in reactivity are a direct result of differences in both the thermodynamics and kinetics of organic reactions on the silicon and germanium surfaces, *the main cause of which is that germanium forms weaker bonds with organic molecules than silicon*. This effect results in binding energies of reaction products on Ge(100)-2×1 that are lower than those on Si(100)-2×1 (with the possible exception of dative-bonded species), typically by a substantial 13 kcal/mol or greater, depending on what types of bonds are formed with the surface. This greatly increases the possibility of eliminating side products through thermodynamic selectivity on the Ge(100)-2×1 surface over the Si(100)-2×1 and C(100)-2×1 surfaces. We note that the dynamics of dimer buckling on Si(100)-2×1 and Ge(100)-2×1 differ at room temperature, with rapid dimer buckling in a flip-flop motion occurring on Si(100)-2×1,[42,43] whereas on Ge(100)-2×1 the dimers are statically buckled.[44] However, in all of the reactions studied, with the possible exception of the [2 + 2] C=C cycloaddition reaction, the dimer is “locked down” in the precursor state by the adsorbed molecule on both Si(100)-2×1 and Ge(100)-2×1 since dative bonding at the “up” dimer atom is calculated to be unstable. Hence, the differences in the dynamics of dimer buckling on Si(100)-2×1 and Ge(100)-2×1 are likely to significantly affect only the dynamics of the initial adsorption into the precursor state.

Due to the strong bonds silicon forms with organics, the reaction products of organics on Si(100)-2×1 are almost always irreversibly stable on the surface and undergo some degree of decomposition upon annealing. This decomposition thwarts attempts to improve thermodynamic selectivity or achieve thermodynamic control by increasing the surface temperature. However, thermodynamic selectivity may be enhanced on silicon for reactions in which aromaticity must be broken (e.g., [4 + 2] and [2 + 2] cycloaddition reactions of benzene), since the product formed will be destabilized by the loss of resonance energy. Another strategy for improving thermodynamic selectivity to eliminate side products on silicon as well as on germanium is to use molecules where the competing reaction products are highly strained or suffer from large steric or electronic effects (e.g., through the use of bulky or electron-withdrawing substitutents).

The weaker bond strengths of organics attached to germanium have important effects on reaction kinetics as well. It is seen from our theoretical calculations that activation barriers are larger on Ge(100)-2×1 than on Si(100)-2×1. Thus, certain reactions which occur on Si(100)-2×1 may be less favorable or even inaccessible at the reaction temperature on Ge(100)-2×1. If the transition state for a precursor-mediated reaction is pushed from below the vacuum level on Si(100)-2×1 to above the vacuum level on Ge(100)-2×1, then the reaction will also have to compete unfavorably with reversible desorption of the precursor state. Thermodynamics may also directly enhance the kinetic selectivity of a reaction by eliminating kinetically competitive reactions whose products are too weakly bound to remain stable at the reaction temperature, as was discussed for the reaction of 2-cyclohexen-1-one on Ge(100)-2×1. Additionally, it is possible for the relative kinetics of two reactions to switch on the Si(100)-2×1 and Ge(100)-2×1 surfaces, depending on the types of bonds being broken and formed at the transition state. An example of this is seen for EVK, where the ene transition state is calculated to be slightly lower in energy than the [2 + 2] C=O cycloaddition transition state on the Si(100)-2×1 surface, while the reverse is true on the Ge(100)-2×1 surface. This could result, for example, in a situation in which one reaction of a multifunctional compound is the observed major pathway on silicon and the minor pathway on germanium, or vice versa.

Because 5-hexen-2-one lacks the conjugation necessary to undergo [4 + 2] cycloaddition reactions, its adsorption behavior provides additional information on the factors affecting competition for the other reactions. Evidence is present for a minor [2 + 2] C=C cycloaddition product on the Ge(100) surface and possibly the Si(100) surface as well, even though its transition state is several kilocalories per mole higher in energy than that of the major ene product. Thus, the 5-hexen-2-one results show that, due to the high reactivity of clean semiconductor surfaces, barrier differences greater than several kilocalories per mole between competing reactions may be necessary for total selectivity. These results suggest that thermodynamic selectivity and thermodynamic control will be important for achieving selectivity rather than relying solely on calculated differences in kinetics.

In summary, this work provides an example of the interplay of both thermodynamic and kinetic factors in governing the reactivity of semiconductor surfaces toward organic molecules. The differences in these factors on Si(100)-2×1 and Ge(100)-2×1 can help explain the differences observed in the competition and selectivity of multifunctional compounds on these surfaces, as demonstrated with this model system of unsaturated ketones. Although we have specifically investigated the (100) faces of Si and Ge in this study, the conclusions drawn concerning selectivity on Ge versus Si should also apply broadly to other faces (e.g., (111)) as well since the bonds formed at different crystal faces should not significantly differ in strength. We note that the selectivity of the attachment of an organic molecule on semiconductor surfaces will depend on the relationship between the competing reactions and will not necessarily be enhanced on Ge relative to Si in every case. *However, it is clear from the theoretical and experimental results of this study that both thermodynamic and kinetic factors favor germanium for the selective attachment of organics over silicon.*

B. [4 + 2] Trans Cycloaddition and Interdimer Reactions. The hetero-Diels−Alder reaction on semiconductor surfaces, as observed here for EVK, can be considered analogous to the Diels−Alder reaction previously reported for 1,3-butadiene and other normal dienes on the C(100)-2×1, Si(100)-2×1, and Ge(100)-2×1 surfaces.[7−9,11,12,23−26,45−50] On the other hand, the

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[4 + 2] trans cycloaddition reaction results in the formation of a trans cyclic product and has no obvious counterparts, to our knowledge, in surface chemistry or organic chemistry. The [4 + 2] cycloaddition reaction of a diene in trans configuration with a C═C bond (e.g., *s-trans*-1,3-butadiene with ethylene) isnot observed since it results in an extremely strained and thermodynamically unfavorable trans cyclic product. We attribute the fact that this reaction is facile on the Si(100)-2×1 and Ge(100)-2×1 surfaces to two main factors. The first and most important of the two is the strength of the reacting π bond of the dienophile, which is broken during the reaction and thus has a direct impact on the reaction energy. While the typical bond strength of an alkene π bond is approximately 63 kcal/mol, the strength of the π bond resulting from the weak overlap of the surface dimer dangling bonds has been estimated to be only around 2−8 kcal/mol on Si(100)-2×1 and Ge(100)-2×1, giving it considerable diradical character.[25,37−40] *Thus, cycloaddition reactions, including [4 + 2] trans cycloaddition, enjoy a substantial thermodynamic advantage of approximately 55−61 kcal/mol with the Si(100) and Ge(100) surfaces relative to alkenes due solely to the weaker dimer π bond versus C═C alkene bond that must be broken*. If the cycloaddition reaction takes place across two surface dimers (i.e., an interdimer reaction), this advantage is decreased slightly to 47−59 kcal/mol due to the cost of breaking an additional dimer π bond.

Another factor which favors the trans cycloaddition reaction on Si(100) and Ge(100) versus alkenes involves the length of the reacting bond of the dienophile. The effect of a longer dienophile bond can be seen by comparing the calculated energies of the one-dimer and interdimer trans reactions, where the distance (before reaction) between the “dienophile” silicon atoms is 2.27 and 3.84 Å, respectively. For the interdimer trans cycloaddition product of EVK on Si(100)-2×1 (Figure 6b), we calculate that 18−24 kcal/mol strain energy is relieved over the one-dimer trans cycloaddition adduct (Figure 6a) after accounting for the cost of breaking an extra dimer π bond. Additionally, we have calculated that for EVK the relative strain of the trans cycloadduct compared to the Diels−Alder adduct is much greater when ethylene, which has a shorter π bond length of 1.33 Å, is the dienophile rather than a Si(100)-2×1 dimer (66 kcal/mol relative strain vs 32 kcal/mol, respectively). Thus, it can be seen from the theoretical results that a longer dienophile bond is correlated with less strain in the trans cyclic product. These results suggest that the trans cycloaddition reaction may be possible in organic/inorganic chemistry between a dienophile with considerable diradical character and a diene which is locked in a trans configuration (to prevent competition from a more favorable Diels−Alder reaction).

Because of the diradical-like nature of the surface dimers, reactions across adjacent surface dimers (i.e., interdimer reactions) can occur which are mechanistically similar to those across a single dimer. For the majority of reactions, particularly those involving addition across adjacent atoms in the reactant molecule (e.g., [2 + 2] cycloaddition) or dissociation (e.g., the N−H dissociation or ene reactions), the interdimer reaction will typically be less favorable than the one-dimer reaction due to the greater distance between the reacting surface atoms and the additional surface π bond that is broken. In some cases, the kinetics and thermodynamics of the interdimer reaction may be comparable to those of the one-dimer reaction, as seen from the calculations of the hetero-Diels−Alder reaction of EVK with Si(100)-2×1 and Ge(100)-2×1. However, the trans cycloaddition reaction of EVK is an example of how interdimer reactions can be more favorable than one-dimer reactions in cases where considerable strain can be relieved. The theory suggests that interdimer reactions may compete with one-dimer reactions, particularly where there is not a substantial strain or barrier penalty associated with the interdimer product. Preventing interdimer reactions in these cases could be a challenging issue for ordered growth.

VIII. Conclusions

We have performed multiple internal reflection infrared spectroscopy studies and density functional theory quantum chemistry calculations on the reaction of a model system of multifunctional unsaturated ketones with the Si(100)-2×1 and Ge(100)-2×1 surfaces. These results have allowed us to examine the factors governing the competition and selectivity of organic reactions on clean semiconductor surfaces. Despite the shared structure and similar electronic character of the Si(100) and Ge(100) surfaces, significant differences in their reactivity with these compounds are observed. The experimental and theoretical results indicate that both ethyl vinyl ketone and 2-cyclohexen-1-one undergo selective [4 + 2] cycloaddition reactions on the Ge(100)-2×1 surface, whereas on the Si(100)-2×1 surface significant ene and possibly [2 + 2] C═O cycloaddition side reactions occur as well.

The greater selectivity of these compounds on the Ge(100) surface versus the Si(100) surface can be explained by differences in both thermodynamic and kinetic factors. While kinetic factors dominate the reaction of organics on the Si surface, thermodynamic factors are also seen to play critical roles on the Ge surface. Due to the weak bonds formed at the Ge surface, the binding energies of some competing reaction products are too weak (e.g., the [2 + 2] C═O cycloaddition product) to remain stably adsorbed on Ge, and the adducts can be selected out. Hence, thermodynamic selectivity is greatly enhanced on the Ge surface relative to the Si surface, where the strong bonds formed typically result in irreversibly adsorbed kinetic products. This fact allows elimination of even kinetically competitive reactions on the basis of their weak, reversible binding and can improve the selectivity of a molecule which has multiple available reaction pathways, as seen with 2-cyclohexen-1-one. Our calculations also show that the barriers for many organic reactions are higher on the Ge surface than on the Si surface. This can lead to improved selectivity by making reactions less kinetically competitive or inaccessible, as seen with ethyl vinyl ketone.

It is clear from the experimental and theoretical results that both thermodynamic and kinetic factors favor Ge over Si for selective attachment. The high reactivity coupled with the lack of thermodynamic selectivity and thermodynamic control on clean silicon surfaces makes selectivity a problematic issue with multifunctional compounds. These results suggest that Ge may

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be a superior material for the selective attachment of organic compounds onto semiconductor surfaces. It is our hope that this work will lead to increased interest in studying the surface chemistry of germanium, which has been largely ignored in comparison with silicon. We believe that the results of this study provide valuable new insights into understanding how clean semiconductor surfaces react with organic molecules which have available to them multiple possible reaction pathways. This understanding will be critical in the design methodology of controlled, selective attachment of organic monolayers onto semiconductor surfaces.

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