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Semiconductor Surface-Induced 1,3-Hydrogen Shift: The Role of Covalent vs Zwitterionic Character

Michael P. Schwartz,[†] Daniel E. Barlow,[‡] John N. Russell, Jr.,*[,‡]
Kevin P. Weidkamp,[†] James E. Butler,[‡] Mark P. D'Evelyn,[§] and Robert J. Hamers*[,†]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, Chemistry Division, U.S. Naval Research Laboratory, Washington, D.C. 20375, and GE Global Research, P.O. Box 8, Schenectady, New York 12301

Received January 25, 2006; E-mail: john.russell@nrl.navy.mil; rjhamers@facstaff.wisc.edu

Abstract: X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) are used to compare the reaction of 1,2-cyclohexanedione (1,2-CHD) with Si(001) and diamond(001) surface dimers under ultra-high-vacuum conditions. 1,2-CHD is known to undergo a keto−enol tautomerization, with the monoenol being the primary equilibrium species in the solid and gas phases. XPS and FTIR data demonstrate that 1,2-CHD reacts with diamond(001) through the OH group of the monoenol, resulting in only one O atom being bonded to the surface. In contrast, XPS and FTIR data suggest that both oxygen atoms in the 1,2-CHD molecule bond via Si−O−C linkages to the Si(001) surface dimer, and that the molecule undergoes an intramolecular 1,3-H shift. While the Si(001) and diamond(001) surfaces are both comprised of surface dimers, the diamond(001) dimer is symmetric, with little charge separation, whereas the Si(001) dimer is tilted and exhibits zwitterionic character. The different reaction products that are observed when clean Si(001) and diamond(001) surfaces are exposed to 1,2-CHD demonstrate the importance of charge separation in promoting a 1,3-H shift and provide new mechanistic insights that may be applicable to a variety of organic reactions.

Introduction

Keto−enol tautomerism plays an important role in many organic reactions. However, while keto−enol chemistry is important, there are very few studies that explore the fundamental nature of keto−enol transformations and associated reactions, primarily due to the difficulty in isolating these molecules in an easily characterized system. As a result, experimental work involving tautomerism is mostly limited to ions in the gas phase[1−8] and indirect experimental procedures in which equilibrium is reached in the liquid phase.[9] Recently, it has been reported that neutral enol species play an important role in hydrocarbon oxidation in flames, illustrating an example of how this incompletely understood class of molecules has unanticipated implications in chemistry.[10,11]

Diamond(001) and Si(001) surfaces offer an interesting comparative model system for studying organic reactions that are influenced by ionic species and/or strained alkenes due to the fundamental structure of the dimers from which these surfaces are composed. Diamond(001) dimers are strained, double-bonded species that exhibit little charge transfer between C atoms, and they have been described as having biradicaloid structure.[12] As a result, chemical reactions with alkene molecules that typically do not occur at room temperature are facile on diamond(001).[13−16] In contrast, Si(001) dimers have been described as having molecular, diradical, and most importantly, zwitterionic character due to charge transfer between atoms,[17−21] and the ionic nature of silicon dimers plays a very important

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[†] University of Wisconsin, Madison.
[‡] U.S. Naval Research Laboratory.
[§] GE Global Research.

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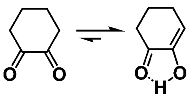
1 

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Figure 1. 1,2-CHD in the **1** diketone and **2** monoenol forms. The molecule exists primarily in form **2** for solid and gas phase (see ref 7).

role in the chemistry of Si(001) surfaces.[16,22−27] Acrylonitrile, a model polar molecule, has been shown to form very different products when reacting with Si(001) compared to diamond(001), demonstrating how dimer structure influences reaction pathways for organic molecules.[16] It might therefore be expected that comparing chemistry on diamond(001) vs Si(001) could offer a generally useful method for studying complicated systems such as keto−enol reactions, in which ionic species may play an important role in product formation.

For this work, we chose to study the influence of group IV (001) surface dimers on a model enol system. While most ketones exist primarily in the keto form, small cyclic 1,2-diones exist almost entirely in the monoenol form in solid and gas phases.[7,28] 1,2-Cyclohexanedione (1,2-CHD) in particular has been used as a model molecule for understanding mechanistic details of keto−enol transformation in aqueous solution.[29−31] 1,2-CHD is shown in the diketone (**1**) and monoenol (**2**) forms in Figure 1. The interaction of 1,2-CHD with diamond(001) and Si(001) represents an interesting system to study, since reactions can be assumed to occur through the monoenol form of the molecule and the difference in dimer structure may influence products in a way that allows fundamental conclusions to be drawn.

Our results show that different products are observed when 1,2-CHD reacts with diamond(001) compared to Si(001). In particular, Si═Si surface dimers induce an H-atom rearrangement within the 1,2-CHD molecule, resulting in a product that is similar to what would be expected for reaction with the diketone form, while C═C surface dimers appear to react directly with the OH bond of the monoenol molecule. An H-atom rearrangement is induced only by the zwitterionic Si═Si surface species and is, to the best of our knowledge, the first experimental evidence for such an uncatalyzed reaction of a neutral enol species. These results demonstrate the usefulness of comparing chemistry on diamond(001) and Si(001) for probing chemical reactions that are influenced by ionic species.

Experimental Methods

Experiments were performed in separate ultra-high-vacuum (UHV) chambers (base pressures $<10^{-10}$ Torr). X-ray photoelectron spectroscopy (XPS) was used to characterize elemental composition and chemical oxidation states. Fourier transform infrared spectroscopy (FTIR) was used to measure vibrational spectra of chemisorbed monolayers and physisorbed molecular multilayers on silicon and diamond (001) surfaces.

Silicon and Diamond Samples. Silicon wafers (purchased from Wacker) used in the XPS and FTIR experiments were oriented to ±0.5° of the (001) plane. Scanning tunneling microscopy measurements show that these samples have large, flat terraces separated by steps that are one atomic layer in height, and have equal amounts of the equivalent (1×2) and (2×1) domains of dimer orientations.[32,33] We used highly Sb-doped ($<0.1\ \Omega$ cm) silicon wafers that were polished on one side for XPS experiments and lightly B-doped ($>5\ \Omega$ cm) silicon wafers that were polished on both sides for FTIR experiments. For XPS experiments, the ~0.5 mm thick silicon samples were cut into ~1 cm × 2 cm rectangles. FTIR spectra were collected on 8 mm × 34 mm × 380 μm Si(001) substrates. For all silicon experiments, a clean (2×1)-reconstructed surface was produced by degassing the samples overnight at 840 K and then flash annealing to 1400 K until the pressure stabilized at $<3\times10^{-10}$ Torr.[32]

Two natural type IIa diamond samples were used (the XPS sample was purchased from Harris International, and the internal reflection element (IRE) sample was provided by General Electric). The major surfaces of each sample were oriented to within 2° of the (001) crystal surface. The sample used for XPS experiments was received as a cut and polished square flat (3 mm × 3 mm × 0.5 mm). The sample used as an IRE for FTIR experiments was received as a cut and polished trapezoidal prism (15 mm × 3 mm × 0.25 mm with 45° bevels on the narrow edges). The prism was held in the UHV system on a molybdenum block, the heating and cooling of which are described elsewhere.[34] For both XPS and FTIR experiments, the diamond surfaces were cleaned in a series of acid baths and subsequently treated with an H-plasma to produce a clean, well-ordered diamond(001)−(2×1) reconstructed, H-terminated surface.[35] The diamonds were then transferred into the UHV systems, where they were heated to ~1375 K in UHV to remove the surface hydrogen and produce a clean diamond(001)−(2×1) reconstructed surface.[36]

Reagents and Dosing. Each vacuum chamber used a stainless steel gas handling system. 1,2-Cyclohexanedione (98% purity, Fisher Scientific) and cyclohexene (>99.7%, Aldrich) were transferred under nitrogen into a glass bulb that was attached to a stainless steel valve and were degassed using three melt−freeze−pump or freeze−pump−thaw cycles, respectively. The reagent purities were verified using mass spectrometry and infrared spectroscopy. The compounds were admitted to the UHV chamber from the gas handling system via a leak valve while the chamber pressure was measured with a nude ionization gauge. Variations between the vacuum systems, especially the location of the leak valves with respect to the samples and ionization gauges, lead to slight differences in the measured and effective dosing pressures of the reactive gases over the substrates. The pressures used in this work were not corrected for these differences and for the ionization gauge sensitivity for each compound. All doses are expressed in langmuirs (L), where $1\ \mathrm{L} = 1\times10^{-6}$ Torr s, and were done with the surface at room temperature, unless otherwise noted.

X-ray Photoelectron Spectroscopy. The silicon and diamond XPS measurements were performed in the same UHV system with a Physical Electronics monochromatized Al Kα source and hemispherical analyzer with a 16-channel detector array. The Si(2p) region was probed using a pass energy of 11.75 eV (0.18 eV analyzer resolution), and the O(1s) and C(1s) regions were probed using a pass energy of 5.85 eV (0.09

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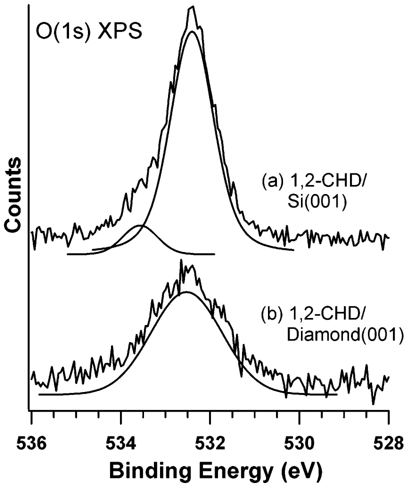

Figure 2. O(1s) spectra for 1,2-CHD adsorbed at 300 K on (a) Si(001) vs (b) diamond(001). The spectrum for 1,2-CHD/Si(001) has two peaks at 532.4 and 533.6 eV. The 1,2-CHD/diamond(001) spectrum contains a single peak at 532.5 eV.

eV resolution). The XPS data were processed using a Shirley background correction,[37] followed by fitting to Voight (Gaussian−Lorentzian convolution) peak shapes. The quality of fit was determined by using a reduced χ^2 statistical analysis. The XPS binding energies for experiments on Si(001) were corrected for slight band bending effects by rigidly shifting all C(1s), O(1s), and Si(2p) peaks so that the Si(2p)$_{3/2}$ and Si(2p)$_{1/2}$ peaks occurred at binding energies of 99.4 and 100.0 eV, respectively. On diamond, all peaks were similarly adjusted using the bulk C(1s) line at 285.0 eV.

Fourier Transform Infrared Spectroscopy. The silicon and diamond FTIR experiments were performed in the same UHV chamber using a Nicolet 800 FTIR spectrometer. FTIR spectra for Si(001) experiments were collected with 8 cm^{-1} resolution in transmission mode at Brewster's angle (74° from normal incidence) using a liquid-nitrogen-cooled MCT-B detector. Multiple internal reflection (MIR) infrared spectra of adsorbates on diamond(001) were collected with 8 cm^{-1} resolution using a liquid-nitrogen-cooled InSb detector. Infrared light from the spectrometer was focused into the UHV chamber through a KBr window and onto one of the beveled edges of the diamond. The light propagated the 15 mm length of the sample via multiple internal reflection, exited the opposite end of the IRE, passed through a slit, and was transmitted through a second KBr window before being focused on the detector.

Results

X-ray Photoelectron Spectroscopy (XPS). Figure 2 shows the O(1s) XPS spectra for (a) a Si(001) surface that has been exposed to 5 L 1,2-CHD at 300 K and (b) a diamond(001) surface that has been exposed to 200 L 1,2-CHD at 300 K. The O(1s) XPS spectrum for 1,2-CHD/Si(001) is characterized by two peaks at 532.4 eV (86% total O(1s) peak area) and 533.6 eV (14%). The peak at 532.4 eV has a binding energy identical to that of the 1,2-CHD/diamond(001) peak (532.5 eV), within the resolution of our instrument. However, the fwhm for the 1,2-CHD/Si(001) peak is 1.2 eV, compared to 1.9 eV for 1,2-CHD/diamond(001). There is also an additional higher binding energy peak for the 1,2-CHD/Si(001) O(1s) spectrum, likely indicating the presence of at least one minority bonding configuration.

Figure 3 shows the O(1s) XPS spectra for a diamond(001) surface that has been exposed to (a) 0.5, (b) 5, (c) 10, (d) 30, (e) 100, and (f) 200 L 1,2-CHD, each at 300 K. Each spectrum is characterized by a single peak at 532.5 eV. The fwhm value ranges from 2.1 eV for the 0.5 L dose to 1.9 eV for the 200 L dose. An evaluation of peak areas for the XPS spectra in Figure 3 also shows that there is no significant change in peak area after a dose of 100 L, indicating that saturation coverage is achieved after a 30−100 L dose.

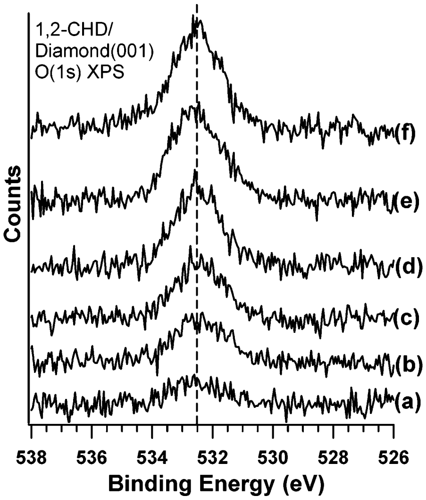

Figure 3. Dose dependence for diamond(001) exposed to (a) 0.5, (b) 5, (c) 10, (d) 30, (e) 100, and (f) 200 L 1,2-CHD, each at 300 K. Each spectrum is characterized by a single peak at 532.5 eV, and the fwhm value narrows from 2.1 eV at low coverage to 1.9 eV at high coverage.

Fourier Transform Infrared Spectroscopy (FTIR). Figure 4 shows FTIR spectra for (a) a multilayer of 1,2-CHD at 90 K on Si(001), (b) 100 L 1,2-CHD dosed on a 300 K Si(001) surface, and (c) a multilayer of cyclohexene at 90 K on Si(001). Figure 5 shows FTIR spectra in the 1630−1700 cm^{-1} region for (a) a multilayer of 1,2-CHD at 90 K on Si(001) and (b) a multilayer of cyclohexene at 90 K on Si(001). The FTIR spectrum for the multilayer of 1,2-CHD at 90 K (Figures 4a and 5a) is characterized by many spectral features, including peaks at 1652 and 1670 cm^{-1} which are likely associated with π-conjugated C═C and C═O absorbance, respectively, alkane C−H stretching peaks at 2833, 2868, and 2939 cm^{-1}, an alkene C−H stretching peak at 3024 cm^{-1}, and a strong, broad peak at 3398 cm^{-1} that is in the region associated with hydrogen-bonded O−H stretching.[38] The 1,2-CHD/Si(001) FTIR spectrum in Figure 4b is characterized by peaks at 1027 and 1190 cm^{-1}, which are in the region associated with Si−O−C, Si−O−Si, or C−OH absorbance,[38] a weak Si−H peak at 2077 cm^{-1}, and C−H stretching modes at 2846, 2862, and 2941 cm^{-1}. The presence of water bands (due to trace amounts of water vapor in the nitrogen purge line outside the chamber) in the 1600−1700 cm^{-1} region for the 1,2-CHD/Si(001) FTIR spectrum obscures any weakly absorbing carbonyl or C═C species. The multilayer of cyclohexene (Figure 4c) is characterized primarily by peaks in the C−H stretching region. In particular, the cyclohexene FTIR spectrum has alkane C−H peaks at 2834, 2857, and 2925 cm^{-1} and an alkene peak at 3020 cm^{-1}.[39] It is notable that the C═C stretching peak at ~1654 cm^{-1} is very weak (it is only visible when the spectrum is enlarged, see Figure

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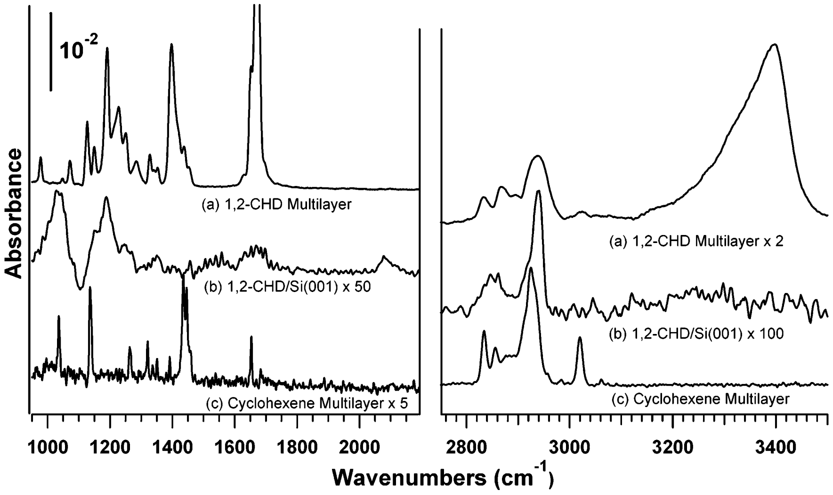


Figure 4. FTIR spectra for (a) a multilayer of 1,2-CHD at 90 K, (b) 100 L 1,2-CHD dosed on a Si(001) surface at 300K, and (c) a multilayer of cyclohexene at 90 K. Each spectrum was collected in transmission mode on a Si(001) sample.

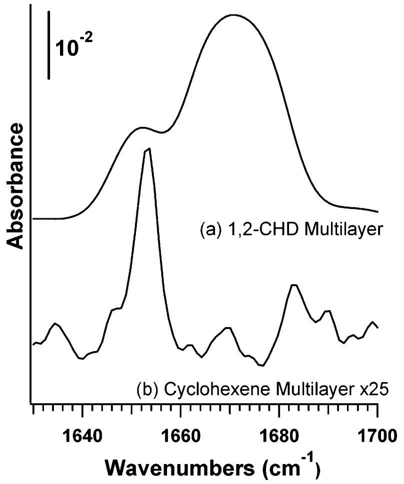


Figure 5. FTIR spectra in the 1630−1700 cm^{-1} region for (a) a multilayer of 1,2-CHD at 90 K and (b) a multilayer of cyclohexene at 90 K. Each spectrum was collected in transmission mode on a Si(001) sample.

Table 1. Observed Infrared Peaks (cm^{-1}) and Assignment

assignment	1,2-CHD/ Si(001)[a]	1,2-CHD/ C(001)[b]	1,2-CHD multilayer	cyclohexene[a,c]
Si−O−C stretch	1027			
	1190			
C=C stretch			1652[a]	1654
C=O stretch			1670[a]	
Si−H stretch	2077			
alkane C−H stretch	2846	2837	2833,[a] 2835[b]	2834
	2862	2875	2868,[a] 2870[b]	2857
	2941	2947	2939,[a] 2943[b]	2925
alkene C−H stretch			3024[a,b]	3020
O−H stretch			3398[a,b]	

[a] Transmission mode on Si(001), MCT-B detector. [b] MIR mode on diamond(001), InSb detector. [c] Assignment from ref 39.

5b), which is consistent with previously reported cyclohexene spectra.[39] Table 1 summarizes the relevant infrared peaks observed for this work.

Figure 6 shows the FTIR spectra in the C−H stretching region for a diamond(001) surface that has been exposed to (a) 5, (b) 20, (c) 30, and (d) 40 L 1,2-CHD at 300 K. Each spectrum is characterized by peaks at 2837, 2875, and 2947 cm^{-1}, all of which are within the region usually associated with alkane C−H

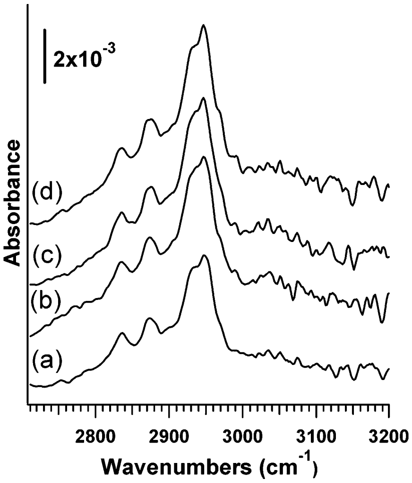


Figure 6. FTIR spectra for a diamond(001) surface that has been exposed to (a) 5, (b) 20, (c) 30, and (d) 40 L 1,2-cyclohexanedione (1,2-CHD) at 300 K. Spectra were collected in MIR mode.

stretching vibrations. On the basis of there being very little change between the spectra in Figure 6c (30 L) and 6d (40 L), we conclude that a diamond(001) surface is saturated with 1,2-CHD after a dose of 30 L, which is consistent with what was observed using XPS measurements.

Discussion

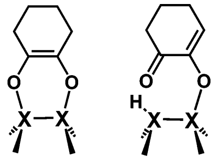
Keto−Enol Tautomerism of 1,2-CHD. Figure 1 shows a schematic representation of 1,2-CHD. While most ketones exist primarily in the keto form (structure **1**), small cyclic 1,2-diones exist almost entirely in the monoenol form (structure **2**) in solid and gas phases.[7,28] The presence of a strong, broad peak at 3398 cm^{-1}, which is consistent with a hydrogen-bonded O−H stretching peak, an alkene C−H stretching peak at 3024 cm^{-1}, and a C=C stretching peak at 1652 cm^{-1} in the FTIR spectrum for a multilayer of 1,2-CHD (Figures 4a and 5a), confirms that solid 1,2-CHD exists primarily in the monoenol form. The multilayer FTIR spectra, combined with gas-phase FTIR data (not shown) and a previous gas-phase study,[7] show that 1,2-CHD exists as the monoenol (structure **2**) and are consistent with 1,2-CHD being in the monoenol form when dosed to the diamond(001) or Si(001) surfaces. This is an important point since the reaction of 1,2-CHD in the monoenol form cannot be considered analogous to that of butadiene, and therefore it is expected that the reaction will be fundamentally different than reactions of dienes on Si(001)[40−42] and diamond(001)[14] surfaces.

Bonding Configuration. (i) 1,2-CHD/Si(001). There are several aspects of the experimental data that help to assign the bonding configuration for 1,2-CHD on Si(001). The presence of two peaks in the O(1s) XPS spectrum indicates that O atoms are present in at least two chemically distinguishable states after a Si(001) surface has been exposed to saturation coverage of 1,2-CHD. The O(1s) XPS peak at 532.4 eV for 1,2-CHD/Si(001) represents 86% of the O atoms present on the Si(001) surface and is similar to an O(1s) peak observed for Si−O−C bonding.[43]

Direct evidence for bonding can be determined by evaluating FTIR spectra (Figures 4 and 5). In particular, upon adsorption to the Si(001) surface, the O−H stretching peak observed at 3398 cm^{-1} for solid 1,2-CHD completely disappears. Furthermore, the strong C=O stretching peak at 1670 cm^{-1} that is observed for the multilayer of 1,2-CHD is almost completely eliminated (a very small peak could potentially be present below the water bands) in the 1,2-CHD/Si(001) spectrum. The combination of loss of O−H and C=O absorbance strongly indicates that both oxygen atoms are involved in bonding 1,2-CHD to the Si(001) surface. Additionally, FTIR peaks are observed at 1027 and 1190 cm^{-1} for 1,2-CHD/Si(001). Several possible chemical species can give rise to significant IR absorbance between 1000 and 1200 cm^{-1}, including C−OH, Si−O−Si, C−O−C, and Si−O−C functional groups.[38] The C−OH species can be ruled out on the basis of the loss of the OH stretch present in the intact molecule, while Si−O−Si and C−O−C would require reaction pathways that include significant molecular dissociation that are unlikely to occur under UHV conditions at 300 K. Therefore, it is likely that the FTIR peaks observed at 1027 and 1190 cm^{-1} are due to Si−O−C vibrations, supporting the idea that O atoms from 1,2-CHD directly bond to the Si(001) surface.

Evidence for changes in the structure of the ring of 1,2-CHD upon adsorption to Si(001) can be found in the C−H stretching region. The FTIR spectrum in the C−H stretching region for 1,2-CHD/Si(001) (Figure 4b) differs in both peak position and intensity compared to the 1,2-CHD multilayer (Figure 4a). Also, while the multilayer of 1,2-CHD shows a weak absorbance above 3000 cm^{-1} that can be attributed to the single alkene C−H stretch, the adsorbed species does not show evidence for any absorbance in this region (although the weakness of the peak combined with the noise of the spectrum may limit our ability to observe such a peak). On the basis of the differences observed in the C−H stretching region, we therefore conclude that the structure of the ring has changed upon adsorption of 1,2-CHD to Si(001).

One possible bonding configuration that is consistent with the XPS and FTIR data for 1,2-CHD adsorption on Si(001) is structure **3**, as shown in Figure 7. For structure **3**, the six-membered ring of 1,2-CHD resembles cyclohexene with the H atoms of the C=C group replaced by −O−Si linkages to the surface dimer. Therefore, it might be expected that the FTIR spectrum for the remaining alkane C−H absorbance would be similar to the alkane C−H absorbance of cyclohexene.



3 **4**

Figure 7. Possible bonding configurations for 1,2-CHD on Si(001) and C(001) surfaces. X = C or Si.

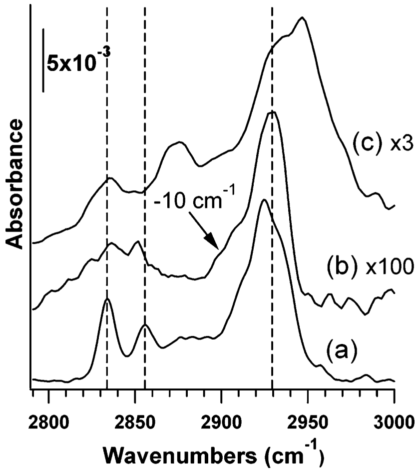


Figure 8. FTIR spectra in the C−H stretching region for (a) cyclohexene, (b) 1,2-CHD on Si(001), in which the entire spectrum is shifted by 10 cm^{-1}, and (c) 1,2-CHD on diamond(001). Spectra (a) and (b) were acquired using transmission mode. Spectrum (c) was collected in MIR mode.

Figure 8 shows a comparison of the CH stretching region for (a) a multilayer of cyclohexene, (b) 1,2-CHD chemisorbed on Si(001), in which the spectrum is shifted lower in frequency by 10 cm^{-1}, and (c) 1,2-CHD adsorbed on diamond(001). FTIR peaks at 2834, 2857, and 2925 cm^{-1} for cyclohexene are similar to peaks that have been attributed to C−H stretching of the four sp^3-hybridized C atoms.[39] The intact cyclohexene FTIR spectrum (Figure 8a) almost exactly overlaps the spectrum for 1,2-CHD/Si(001) after a 10 cm^{-1} shift (Figure 8b), within the noise of our data. Since small changes in ring structure usually lead to significant differences in spacing and peak intensity, the similarity in relative position and intensity of FTIR peaks for 1,2-CHD/Si(001) compared to those for cyclohexene suggests that the structure of the ring is the same for the two species.

It might be expected that a C=C peak would be observed in the 1600−1700 cm^{-1} region for structure **3**, since the intact 1,2-CHD molecule shows a strong absorbance at 1652 cm^{-1} due to C=C absorbance (see Figure 5a). The strength of the C=C absorbance peak for the intact 1,2-CHD molecule can be attributed to the fact that the C=C bond is conjugated to a C=O bond.[38] However, symmetric C=C bonds only weakly absorb in the infrared,[38] which explains why C=C absorbance for cyclohexene (see Figure 5b for expanded spectrum) is very weak. Therefore, it is reasonable that we would not observe C=C absorbance for 1,2-CHD/Si(001) if the bonding configuration is structure **3**. On the basis of the presence of a primary bonding configuration that has a majority of the O atoms in

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similar oxidative states, changes in ring structure that lead to FTIR absorbance that is similar to that of cyclohexene, and FTIR evidence for both O atoms being involved in bonding directly to Si atoms, we conclude that 1,2-CHD reacts with a Si═Si dimer to form structure **3** (Figure 7).

In addition to the primary species for 1,2-CHD/Si(001), a minority species is also present, as indicated by an O(1s) XPS peak at 533.6 eV which represents 14% of the total surface-bound O atoms. Therefore, as much as 28% of the 1,2-CHD molecules could be bound into a minority configuration(s) since there are two O atoms that need to be accounted for in the intact molecule (the upper limit being the case where a second peak overlaps with the peak at 532.4 eV). One possible minority species for 1,2-CHD/Si(001) might be one in which the OH group dissociates across a Si═Si dimer (such as structure **4**, Figure 7), which could account for the small amount of observed Si−H absorbance in the FTIR spectrum. However, the lack of a significant peak in the C═O stretching region suggests that only a very small fraction of the molecules could form a minority species such as structure **4**, which is consistent with the observation that the Si−H FTIR peak is weak. Also, C═O and Si−O−C species are expected to lead to similar O(1s) binding energies,[43−46] which seems to indicate that the higher energy O(1s) XPS peak is not due a bonding configuration such as structure **4**.

The fact that the O(1s) XPS peak for 1,2-CHD/Si(001) is found at higher binding energy than for the majority configuration suggests that O atoms are in a more electron-deficient environment than for the Si−O−C species, and may indicate the presence of a dative-bonded precursor state (see Figure 10). Initial interaction between the C═O or OH groups and a Si═Si dimer to form a dative-bonded state would be analogous to what has been observed previously for amines[23,25,47,48] and phosphines.[49] A dative-bonded state has been predicted for carbonyl-containing molecules on Si(001)[50,51] and observed experimentally on Ge(001),[52] and an OH dative-bonded state has been predicted for water[53] and methanol[54] on Si(001). More recently, an O(1s) XPS peak at 532.9 eV has been attributed to a species in which carbonyl O-atom lone-pair electrons are donated to a Ge═Ge dimer for acetyl chloride adsorbed on Ge-(001).[55] Our observation of an O(1s) peak at 533.6 eV for 1,2-CHD/Si(001) indicates that the O atom is in a more electron-deficient state than what was observed for the acetyl chloride/Ge(001) system,[55] which would be consistent with a dative-bonded intermediate.

(ii) 1,2-CHD/Diamond(001). A comparison between the FTIR spectra in the C−H stretching region for 1,2-CHD adsorbed on Si(001) (Figure 8b) and diamond(001) (Figure 8c) reveals differences in both relative peak position and intensity, suggesting that the chemical species on each surface is also different. The O(1s) XPS spectrum for 1,2-CHD/diamond(001) is characterized by a single, broad peak centered at 532.5 eV. The presence of a single peak for XPS spectra normally indicates a single oxidative state. However, the large fwhm value of 1.9 eV, which is broader than typically observed for single oxidative states using our system, suggests that there may be two narrowly separated peaks near 532.5 eV. If there are two closely spaced peaks for the O(1s) XPS spectrum, the fact that the fitted curve is symmetric (based on the fit to a single peak) indicates that the area and shape of each peak are identical. Therefore, we believe that the symmetry of the O(1s) XPS peak, combined with broadening relative to that expected for a single oxidative state, indicates that 1,2-CHD adsorbs to diamond(001) through a single bonding configuration containing two O atoms with different oxidative states.

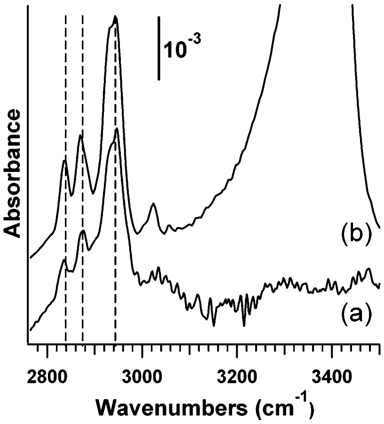

Figure 9. Comparison of FTIR spectra for (a) 1,2-CHD adsorbed on diamond(001) at 300 K and (b) a 1,2-CHD multilayer at 90 K. Spectra were acquired using MIR mode.

Figure 9 shows a detailed comparison of the FTIR spectra for (a) 1,2-CHD/diamond(001) at 300 K and (b) a multilayer of 1,2-CHD, each collected in MIR mode. The spectrum for 1,2-CHD/diamond(001) is characterized by alkane C−H peaks at 2837, 2875, and 2947 cm^{-1}, identical within the resolution of the experiment to the peaks at 2835, 2870, and 2943 cm^{-1} for the multilayer. The fact that the CH stretching region is identical for 1,2-CHD/diamond(001) and the intact 1,2-CHD molecule indicates that the ring remains unperturbed upon adsorption to the diamond(001) surface. Furthermore, the absence of an O−H peak for 1,2-CHD/diamond(001) indicates that 1,2-CHD reacts with a C═C surface dimer through cleavage of the O−H bond, which is consistent with previous observations of water dissociative adsorption on diamond(001).[56]

While O−H cleavage would result in H atoms adsorbed on diamond(001), the C−H stretch of the adsorbed H atoms overlap those of the molecule itself. However, since only one H atom per adsorbed molecule would be bonded to a C═C dimer, the contribution to C−H absorbance would likely be small. An alkene C−H stretching mode is observed for the intact 1,2-CHD molecule, and a broad alkene C−H mode may be present at ∼3050 cm^{-1} for the adsorbed species, but a strong diamond three-phonon absorption results in low signal/noise in this

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spectral region, making this assignment tenuous. The diamond is opaque in the carbonyl stretching region due to two-phonon absorption, and therefore C═O absorbance cannot be observed. Nevertheless, on the basis of XPS data that indicate a single bonding configuration, the strong similarity of the alkane C−H stretching modes between the 1,2-CHD multilayer and the adsorbed species, and the absence of the O−H stretch upon adsorption, we conclude that 1,2-CHD reacts with diamond(001) to form structure **4** (Figure 7).

Mechanism. XPS and FTIR data reveal that 1,2-CHD reacts with the Si(001) and diamond(001) surfaces to produce different adsorption products. The Si(001) surface causes 1,2-CHD to undergo a 1,3-H shift, while the diamond(001) surface induces cleavage of the O−H bond such that the H atom is removed from the 1,2-CHD molecule but the general structure of the ring remains intact. To understand this difference in reactivity, we first note that both Si(001) and diamond(001) surfaces have the same basic structure, consisting of pairs of atoms bonded to one another as a dimer unit. While both Si(001) and diamond(001) dimers can be described in terms of a strong σ-bond and a weak π-bond, there are significant differences in their chemistry. Primarily, tilting of Si═Si dimers out of the surface plane is accompanied by significant transfer of electron density from the "down" to the "up" atom, giving rise to zwitterionic character that is reflected in an ability to act as both an electron donor and an electron acceptor.[23,25,47,48] Diamond dimers are better described as symmetric, with little charge transfer between C atoms.[12,57−60] As a result of dimer structure differences, diamond(001) has been found to be less reactive than Si(001),[13,14] and acrylonitrile has been shown to form very different reaction products on Si═Si and C═C surface dimers.[16]

The electron-accepting ability of Si(001) likely plays a key role in controlling reactivity with 1,2-CHD. 1,3-H shifts have been observed for gas-phase ions in mass spectrometry,[2−5,8] but not for an uncatalyzed neutral molecule, indicating that the charge state of keto−enol species plays an important role in whether a molecular 1,3-H shift can occur. Figure 10 shows one potential mechanism for the reaction of 1,2-CHD with a Si═Si dimer. The initial step involves donation of lone-pair electrons from the carbonyl O atom to the down end of a Si═Si dimer, leading to the formation of a dative-bonded intermediate state, similar to those predicted and observed for a number of systems on Si and Ge surfaces.[23,25,47−54] After initial formation of a dative bond, transfer of the H atom and reaction of the second O atom with the electronegative end of the Si═Si dimer would lead to the observed primary bonding species.

The O(1s) XPS peak for 1,2-CHD/Si(001) at higher binding energy than that observed for the primary bonding configuration may indicate the presence of a stable dative-bonded species. Dative-bonded states for water on Si(001)[53] and acetic acid on Ge(001)[61] have been predicted to be stabilized by hydrogen bonding to the electronegative end of a surface dimer. In the case of acetic acid on Ge(001), the hydrogen-bonded state leads to delocalization of π-orbitals between the molecule and the surface,[61] and it might be possible that a dative-bonded state for 1,2-CHD/Si(001) could be stabilized by a similar effect. In the present case for 1,2-CHD/Si(001), additional stabilization might be provided by delocalization of charge within the conjugated π-bonds of the molecule itself (Figure 10), an effect that may also play a key role in inducing the 1,3-H shift.

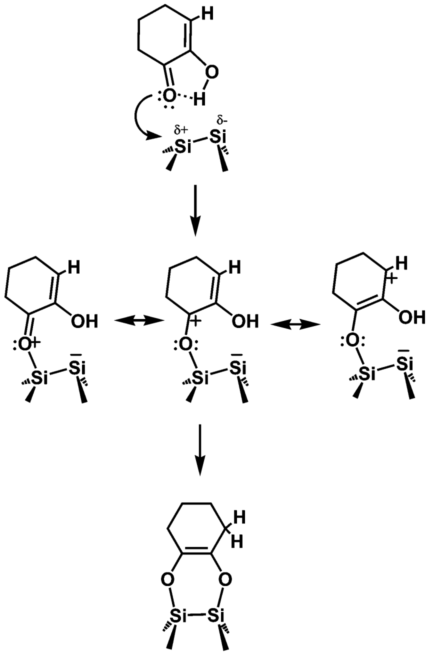

Figure 10. Possible mechanism for reaction of 1,2-CHD with a Si═Si dimer. In the first step, lone-pair electrons from the carbonyl oxygen are donated to the down (electropositive) end of a Si═Si dimer. Charge delocalization may play a role in inducing the 1,3-H shift and reaction of the second O atom with the other end of the Si═Si dimer. A mechanism in which initial attack occurs through the enol O atom could also be envisioned.

Reaction of 1,2-CHD with diamond(001) is fundamentally different than for Si(001) since C═C dimers do not facilitate charge transfer, eliminating the mechanism in Figure 10 as a possible reaction pathway. In fact, a C═C surface dimer reacts directly with the OH bond of a 1,2-CHD molecule to form structure **4** (Figure 7), similar to what has been observed previously for water dissociation on diamond(001).[56] Regardless of the exact reaction pathway for 1,2-CHD bonding to Si(001) compared to C(001), it is clear that the relative ability of a surface dimer to facilitate charge transfer plays a key role in determining the final bonding configuration.

Suprafacial 1,3-H shifts are forbidden by Woodward−Hoffmann (WH) symmetry rules.[62] However, it has been predicted theoretically that a suprafacial 1,3-H shift can occur for neutral C_2H_4O (even though symmetry forbidden) and that the C_2H_4O radical ion species avoids WH constraints.[63] Previously, "forbidden" reactions were facilitated on Si(001) through a low-symmetry intermediate, in which WH constraints were avoided because of the zwitterionic structure of the Si═Si dimers.[27,42,64] Because a 1,3-H shift is observed when 1,2-CHD reacts with Si(001), but not diamond(001), charge transfer appears to be an important element for inducing such a reaction, either by forming an intermediate that avoids WH constraints or by inducing the molecule to distort such that WH transitions are allowed.

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Conclusion

In this work, we have studied the reaction of 1,2-CHD with diamond(001) and Si(001) surfaces. FTIR and XPS data indicate that the product formed when 1,2-CHD reacts with diamond(001) is different than that observed for reaction with Si(001). In particular, while 1,2-CHD reacts with diamond(001) through the OH portion of the monoenol species via OH cleavage, Si(001) preferentially induces a 1,3-H shift within the 1,2-CHD molecule, resulting in a product that involves both O atoms. The different products formed by 1,2-CHD on diamond(001) vs Si(001) can be attributed to differences in the dimer structures on the two surfaces. One important conclusion that can be drawn from these results is the fact that the zwitterionic Si═Si dimer induces an intramolecular 1,3-H shift, suggesting that charge-transfer effects are an important element of uncatalyzed enol–keto transformations. To our knowledge, this work reports the first experimental observation of a surface-induced 1,3-H shift.

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