Cycloaddition Chemistry at Surfaces: Reaction of Alkenes with the Diamond(001)-2 × 1 Surface

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The (001) surfaces of diamond, silicon, and germanium share a similar bonding motif in which pairs of atoms bond to each other via a strong σ bond and a weaker π bond, forming "dimers". The presence of formal double bonds in these dimers suggests that the chemistry of Si(001), Ge(001), and diamond(001) surfaces might show some similarity to the chemistry of compounds such as alkenes and disilenes, which contain C═C or Si═Si double bonds. Indeed, alkenes can bond to Si(001)[1−4] and Ge(001)[5,6] surfaces via the surface analogue of a [2 + 2] cycloaddition. In these "[2 + 2]" reactions the π bond of an alkene and the weak π bond of a surface dimer are broken and two new σ bonds are formed, linking the alkene to the surface through a four-member ring. Conjugated dienes can also react with Si(001) to produce a [4 + 2] "Diels−Alder" product,[4] but with some [2 + 2] products.[7]

Surprisingly, [2 + 2] reactions on Si and Ge surfaces are facile (nearly unity reaction probability per molecule−surface collision), despite the fact that bond formation via a high-symmetry geometry is forbidden.[8−10] The facile nature of [2 + 2] cycloaddition reactions on Si and Ge surfaces could arise from the unique chemistry of these elements, or from intrinsic differences between *surface* dimers and their molecular analogues. The diamond(001) surface provides a crucial test because it consists of C atoms paired into C═C dimers with a partial π bond.[11−14] This surface is therefore an extended array of alkene-like C═C bonds, but with a distorted surface geometry like those at Si and Ge(001) surfaces. Here, we show that diamond(001) surfaces undergo [2 + 2] cycloaddition reactions with a prototypical alkene, cyclopentene, and we compare the nature of [2 + 2] cycloaddition reactions on C, Si, and Ge surfaces.

Experiments on diamond(001) were carried out at the Naval Research Laboratory using an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. A trapezoidal, type IIA, natural diamond ($15 \times 3 \times 0.25$ mm^3) prism, with the large faces oriented to (001) within 2°, was used in a multiple internal reflection geometry. Infrared light from a Fourier transform infrared (FTIR) spectrometer was coupled to the diamond in the UHV chamber through KBr windows and detected using InSb detector. Heating, cooling, and temperature measurement are described elsewhere.[15] Prior to insertion into the chamber, the diamond was cleaned in a series of acids to remove metals and graphitic carbon, followed by a 30-minute treatment with a H-atom microwave plasma, producing a smoothed, hydrogen-capped C(001)−(2 × 1) surface.[16,17] The diamond was transferred to the UHV chamber and heated to 1375 K to remove the hydrogen, leaving a clean (2 × 1)-reconstructed surface.[16] Experiments on Ge and Si were performed at Wisconsin in a similar apparatus.[2] Cyclopentene (Aldrich, purity 99+%) was degassed using four freeze−pump−thaw cycles and introduced through a leak valve.

Figure 1a shows an FTIR spectrum acquired after a clean diamond(001)-2 × 1 surface was exposed to 10 000 langmuirs (1×10^{-5} Torr for 1000 s) of cyclopentene at 300 K. The spectrum shows one large peak at 2953 cm^{-1} with shoulders at higher and lower frequency, and a second, smaller peak near 2880 cm^{-1}. Experiments over a range of exposures showed that the infrared intensity increased up to exposures of ~5000 langmuirs; higher exposures yielded no significant changes in line shape or intensity, indicating that Figure 1a is representative of the saturated surface. Figure 1b, for example, shows a spectrum obtained after 20 000 langmuirs exposure, revealing nearly identical features. Heating the sample to 573 K for 120 s to eliminate any (possibly) physisorbed molecules produced no changes. We also found that H bonded directly to the C(001) surface produces sharp peaks at 2898 and 2919 cm^{-1} with an intensity ratio of ~2:1;[18] since these frequencies are distinct from those observed for chemisorbed cyclopentene, we attribute the peaks in Figure 1a and b to intact cyclopentene molecules chemically bonded to the diamond. The spectra of chemisorbed cyclopentene molecules (Figure 1a, b) are also very different from those of multilayers. Figure 1c shows a spectrum of a multilayer film of cyclopentene, prepared in situ by exposing the cold (90 K) diamond(001) surface to 5 langmuirs of cyclopentene. The 3040 cm^{-1} peak in the condensed multilayer arises from the alkene-like ═C−H stretching vibrations; the almost complete absence of this peak in the chemisorbed monolayer (Figure 1a, b) indicates that the cyclopentene C═C bond is involved directly in bonding to the surface.

Figure 1 also shows spectra of cyclopentene bonded to Si(001) (Figure 1d) and Ge(001) (Figure 1e) surfaces; the [2 + 2] cycloaddition of cyclopentene to these surfaces has been confirmed previously and is evidenced (in part) by the absence of high-frequency alkene C−H vibrations.[2,6] Additionally, the donation of electron density from Si or Ge to the "alkene" C atoms reduces the vibrational frequency of the attached H atoms, producing the C−H vibrational modes at 2840−2860 cm^{-1}. In contrast, bonding to diamond involves no charge transfer; consequently no such low-frequency modes are expected for [2

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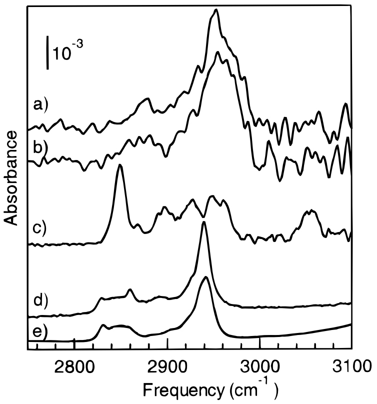

Figure 1. Unpolarized infrared spectra of cyclopentene on C(001), Si(001), and Ge(001) surfaces. (a) Spectrum of C(001) after exposure to 10 000 langmuirs of cyclopentene, 300K. (b) Spectrum of C(001) after exposure to 20 000 Langmuirs of cyclopentene, 300 K. (c) Spectrum of cyclopentene multilayer condensed onto C(001) surface at 90 K. (d) Spectrum of Si(001) after exposure to 10 langmuirs of cyclopentene, 300 K. (e) Spectrum of Ge(001) after exposure to 10 langmuirs of cyclopentene, 300 K.

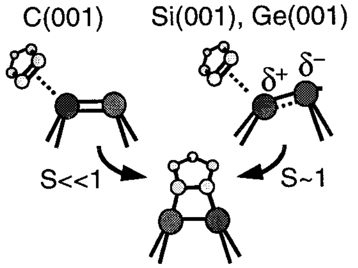

Figure 2. Schematic illustration of the low-symmetry approach of cyclopentene to a surface dimer of Si, Ge, or C and the formation of a low-symmetry intermediate via the interaction of the dimer π^* antibonding orbital with the electron-deficient region of the alkene. Dimer tilting, as depicted at right, increases stability of the intermediate and enhances reaction probability on Si and Ge surfaces, while the tendency of C dimers to remain parallel to the surface leads to a higher reaction barrier and lower sticking coefficient.

+ 2] cycloaddition to diamond, in agreement with our observations. The increased breadth of the spectra on diamond probably arises from stronger intermolecular interactions and greater inhomogeneity of the diamond surface.

The primary result of our experiments is the demonstration that cyclopentene reacts with the C(001)-2 $\times$ *1 surface, yielding a product identical to that expected from a [2 + 2] cycloaddition reaction.*

While C(001), Si(001), and Ge(001) all show similar reaction products, the reactive sticking probabilities are different: by measuring the increase in vibrational intensity with increasing exposure, we have determined that the sticking coefficients for cyclopentene are approximately unity on Si[2], 0.1 on Ge,[6] and on the order of 10^{-3} on diamond. The low (but readily measurable) reaction probability on diamond is attributed to several factors. The barrier associated with "forbidden" [2 + 2] cycloaddition reactions should depend strongly on the $\pi-\pi^*$ splitting of reactants.[8] The relative reaction rates of C(diamond) $\ll$ Ge $<$ Si correlate (negatively) with the ordering of $\pi-\pi^*$ surface-state band gaps of 3.5 eV (350 kJ/mol) for diamond(001),[19] 1.4 eV (140 kJ/mol) for Ge(001),[20] and ~1.1 eV (110 kJ/mol) for Si(001).[21] The low reaction rate on diamond can also be related to the strengths of the surface π bonds: the π bond strength on diamond(001) is ~0.5−0.9 eV (50−90 kJ/mol),[12] smaller than the value of ~2.6 eV (250 kJ/mol) for a typical alkene[22] but larger than the 0.1−0.2 eV (10−20 kJ/mol) values estimated for Ge(001)[23] and Si(001).[24]

The unique *geometry* of the surface dimers also plays an important role in controlling reactivity. On all three surfaces the bonds between the dimers and the underlying bulk are bent away from planarity, causing the π^* orbital at the dimer ends to be accessible to nucleophilic reactants.[9] To test this, we performed ab initio calculations of cyclopentene interacting with 9-atom and 15-atom clusters representing C(001), Si(001), and Ge(001) surfaces. In each calculation a cyclopentene molecule was placed near the surface; and a *local* geometry optimization was performed using Gaussian 98 with the 6-31+G* basis set and the Becke3LYP density functional.[25] These calculations show that cyclopentene can bond to Si(001) and Ge(001) surfaces with little or no barrier through a low-symmetry intermediate, as in Figure 2. On Si and Ge this pathway is facilitated by the ability of Si=Si and Ge=Ge dimers to tilt out of the surface plane, which transfers electron density from the "down" atom to the "up" atom of the dimer.[9,26] On C(001), however, no dimer tilting is present on the clean surface;[12,19] our calculations show no significant tilting induced by interaction with nearby alkenes, thereby leading to a higher activation barrier and a smaller reaction probability.

These experiments show that cycloaddition reactions analogous to those observed previously on Si and Ge surfaces also take place on diamond (001) surfaces. The lower reaction probability on diamond(001) is likely associated with its larger band gap and the absence of dimer tilting, which facilitates the ability of impinging molecules to find a low-symmetry pathway to the final [2 + 2] reaction product on Si and Ge. Our results show that reactivity trends for group IV semiconductor surfaces can be understood using concepts from organic chemistry, and that surface species show behavior that is intrinsically different from their bulk analogues due to the unique geometric deformations at the surface.

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