744 *J. Am. Chem. Soc.* **2000,** *122,* 744−745

Functionalization of Diamond(100) by Diels−Alder Chemistry

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Received August 20, 1999

Diels−Alder reactions are powerful, widely used reactions for C−C bond formation. In addition to the well-known Diels−Alder reactions in the solution phase, it has been shown that they occur on nanoparticles such as C_{60}.[1] In this work, we show that this reaction is also applicable to carbon in the form of an extended covalent solid, specifically the hydrogen-free diamond(100)-2 × 1 surface.

Diamond has recently attracted much attention as a candidate for a wide range of technological applications due to its unique combination of material properties, including high thermal conductivity, hardness, chemical inertness, wide band gap, high carrier mobility, and multispectral optical transparency.[2] Like the other Group IV surfaces of Si(100) and Ge(100), the bare diamond(100) surface undergoes a 2 × 1 reconstruction in which pairs of atoms are bonded into dimers via a strong σ bond and a partial π bond.[3] Recent studies have shown that the surface dimers of Si(100)-2 × 1[4] and Ge(100)-2 × 1[5] can react with conjugated dienes through an analogue of the familiar Diels−Alder [4 + 2] cycloaddition reaction, forming six-membered-ring products at the surface. Alkenes have also been shown to react with the Si(100)[6] and Ge(100)[7] surfaces to form [2 + 2] cycloaddition products.

In this study we investigate the ability of the diamond(100) surface to undergo cycloaddition reactions with a prototypical diene, 1,3-butadiene. We will show that the surface dimer of diamond(100) behaves like a C═C double bond toward organic reactions, and reacts with 1,3-butadiene to form a Diels−Alder adduct directly analogous to molecular cyclohexene.

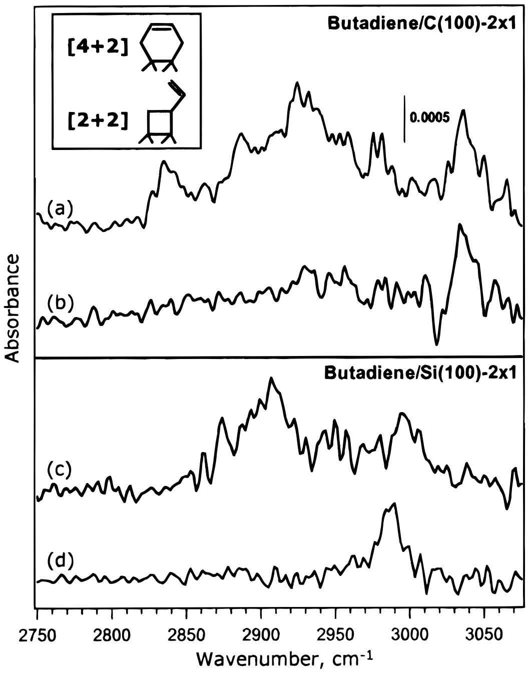

Figure 1. Infrared spectra of 1,3-butadiene adsorbed on the C(100)-2 × 1 and Si(100)-2 × 1 surfaces: (a) 1,3-butadiene (1000 L) on C(100) at room temperature; (b) 1,3-butadiene-*1,1,4,4-d*$_4$ (20000 L) on C(100) at room temperature; (c) 1,3-butadiene (1 L) on Si(100) at room temperature; (d) 1,3-butadiene-*1,1,4,4-d*$_4$ (1 L) on Si(100) at room temperature. Inset: Drawings of the possible reaction products.

Experiments were carried out at the Naval Research Laboratory in an ultrahigh vacuum chamber with a base pressure of 1×10^{-10} Torr.[8] The sample used was a trapezoid-shaped type IIa natural diamond ($15 \times 3 \times 0.25$ mm^3) single crystal designed for multiple internal reflection infrared spectroscopy. Unpolarized light from a Fourier transform infrared (FTIR) spectrometer was focused through one of the beveled edges of the sample, undergoing 33 internal reflections from the two large crystal faces before being collected by a mirror and focused onto an InSb detector external to the chamber. Prior to insertion into the chamber, the sample was cleaned in a sequence of acid mixtures to remove metal, nondiamond carbon, and Si/SiO$_2$ contaminants.[9] The sample was then exposed to a hydrogen microwave plasma for 30 min on each of the two large faces to produce a smooth, 2 × 1 reconstructed (100) surface which is hydrogen terminated and stable in air.[10] Following plasma treatment, the diamond was transferred to the ultrahigh vacuum chamber and heated to 1310 K, removing the hydrogen and leaving the clean 2 × 1 reconstructed surface.[3a,c,11] The prism was opaque in the C−D stretching region due to 2-phonon absorption of the bulk.[12]

Figure 1a shows the infrared spectrum of the C(100)-2 × 1 surface after a 1000 L dose of 1,3-butadiene at room temperature. Several peaks can be seen in the C−H stretching region associated

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10.1021/ja993024i CCC: $19.00

with sp^3 (2800−3000 cm^{-1}) and sp^2 (3000−3100 cm^{-1}) hybridized carbon, indicating adsorption of the butadiene. Comparison with a multilayer spectrum of butadiene adsorbed at 90 K (not shown) confirms that butadiene is chemisorbed to the surface at room temperature rather than physisorbed, based on the markedly different spectra. The absence in Figure 1a of a sharp doublet at 2898 and 2919 cm^{-1}, which are characteristic of hydrogen on C(100),[13] further suggests that chemisorption is nondissociative.

To assign the chemisorbed product, an isotopic substitution experiment using 1,3-butadiene-*1,1,4,4-d*$_4$ ($CD_2{=}CH{-}CH{=}CD_2$) was performed. Figure 1b shows the infrared spectrum of the C(100)-2 × 1 surface after dosing 1,3-butadiene-*1,1,4,4-d*$_4$ at room temperature. The only feature remaining in the deuterated spectrum is the highest energy mode at 3035 cm^{-1}. If a [2 + 2] product were formed upon chemisorption, the highest wavenumber ν(C−H) mode would originate from the terminal $=CH_2$ stretch, while for the [4 + 2] product it stems from the H−C=C−H stretch. However, in 1,3-butadiene-*1,1,4,4-d*$_4$ the terminal CH_2 group is substituted with deuterium, and hence this terminal stretch for a [2 + 2] product would be shifted down to the C−D stretch region near 2200 cm^{-1}. *Because the sp*^{2} *feature remains at 3035 cm*$^{-1}$ *in Figure 1b, we conclude that butadiene forms predominantly the [4 + 2] product on C(100)-2 × 1.* The observation of two small bumps in the spectrum of Figure 1b at around 2930 and 2950 cm^{-1} may signify the presence of secondary product at the surface. One possibility is a minor [2 + 2] side product, since the deuterated [2 + 2] product would have sp^3 ν(C−H) modes in this wavenumber range while the deuterated [4 + 2] product would not. Although a second layer [4 + 2] reaction of deuterated butadiene with the surface adduct would also contain sp^3 ν(C−H) modes, we note that this reaction has not been previously observed on Si[4a] or Ge[5a] and is probably kinetically unfavorable under the experimental conditions of room temperature and low pressure.

The infrared spectra of butadiene and 1,3-butadiene-*1,1,4,4-d*$_4$ chemisorbed on Si(100)-2 × 1[4a] are shown in parts c and d of Figure 1 for comparison. The shapes of the spectra of butadiene on Si(100) resemble that of butadiene on C(100), although the peak positions on Si(100) are shifted down in frequency from C(100). This shift may be related to differences in ring strain in the adduct resulting from the greater length of the Si dimer bond (∼2.2 Å)[14] compared to the C dimer (∼1.4 Å)[3c], or to electron donation effects from the surface of Si versus C. Hence, the adsorption behavior of 1,3-butadiene on C(100) and Si(100) is similar, with both forming the [4 + 2] adduct as the major product. However, coverage studies show that higher dosages of butadiene (∼1−2 orders of magnitude) are required on C(100) than Si(100) to obtain saturation, indicating that the reaction is much less facile on the diamond surface.[15] The lower reactivity of the C(100) surface with butadiene is likely the consequence of a stronger π bond: ca. 50−90 kJ/mol[3c,16] compared to 10−25 kJ/mol[14] on Si(100).

The [4 + 2] reaction of 1,3-butadiene and a C(100)-2 × 1 surface dimer leads to an adduct resembling cyclohexene, as shown in the inset of Figure 1. Given their similarity, it is instructive to compare the infrared spectrum of the chemisorbed [4 + 2] adduct with that of molecular cyclohexene. *There is a striking correlation between the spectrum of physisorbed cyclohexene and that of butadiene chemisorbed on the diamond(100) surface, shown in Figure 2.* The close agreement between the spectra is quite surprising and represents potentially unprecedented agreement between a surface adduct and its molecular analogue. While the spectral similarities provide further evidence that a [4 + 2] surface adduct is formed on C(100), they also introduce provoking questions. For example, although the Diels−Alder product lacks the four C4 and C5 hydrogens of cyclohexene, it exhibits modes at 2860 and 2930 cm^{-1} which have been previously assigned to the C4 and C5 CH_2 stretching modes of cyclohexene.[17] These additional peaks in the adsorbate spectrum may arise from overtones or combination bands, or alternatively they may imply either that multiple conformations of the Diels−Alder product are formed at the surface or that a side product is also present. However, because there is no a priori reason to expect that the absorption spectrum of another product would match so well with molecular cyclohexene, the close correspondence of these features with peaks in the cyclohexene spectrum remains an intriguing issue that would benefit from further study.

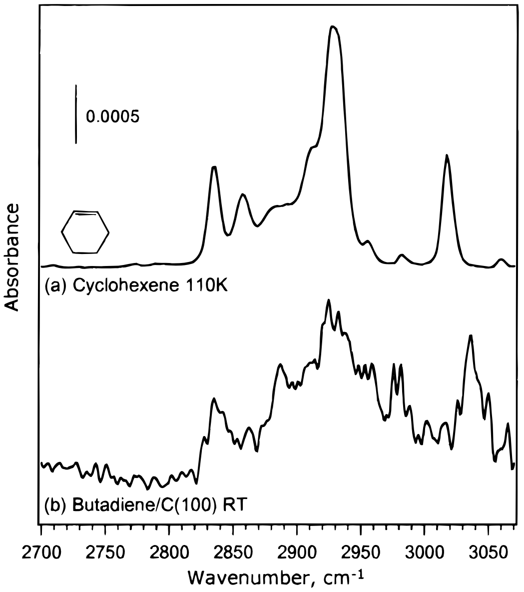

Figure 2. Infrared spectra of (a) physisorbed cyclohexene multilayers at 110 K; (b) 1,3-butadiene on C(100) at room temperature.

In conclusion, we have shown that a prototypical diene, 1,3-butadiene, reacts with the diamond(100)-2 × 1 surface to form a Diels−Alder adduct analogous to cyclohexene. Our results indicate that the surface dimers of diamond(100) can react as carbon double bonds, forming surface adducts that can be directly compared with their free molecular analogues. The results demonstrate a new mechanism for functionalizing the diamond surface, and advance the concept of using organic reactions to attach groups to the surface in a controlled fashion.

Acknowledgment. We are grateful to Jennifer Hovis and Robert Hamers for their contribution to these studies. We thank Collin Mui for insightful discussion and suggestions. G.T.W. acknowledges financial support from a National Science Foundation (NSF) Graduate fellowship. S.F.B. acknowledges financial support from a NSF CAREER award (DMR-9896333) and from the Beckman Foundation. S.F.B. is a Camille Dreyfus Teacher-Scholar. J.N.R. and J.E.B. acknowledge support from the U.S. Office of Naval Research.

JA993024I

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