

Vibrational Spectroscopic Studies of Diels–Alder Reactions with the Si(100)-2×1 Surface as a Dienophile

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Over the last decade, reactions of hydrocarbons on silicon surfaces have received serious attention.¹ One reason for this activity is an interest in understanding how the spatial localization of electron density on surfaces of semiconductors affects the reactivity.² However, whereas interaction of simple unsaturated compounds (such as ethylene and acetylene) has been studied extensively,^{3–7} very little attention has been given to more complicated systems.

In this study we investigate the possibility of a Diels–Alder type [4 + 2] cycloaddition reaction between dienes and the silicon dimers of a Si(100)-2×1 surface, which was theoretically predicted by Konecny and Doren.⁸ Studies of cyclohexadienes on a Si(111)-7×7 surface have been previously reported;^{9,10} however, these studies did not aim at identifying the products of a [4 + 2] cycloaddition reaction, which most likely does not occur on a Si(111)-7×7 surface. On the other hand, the Si(100)-2×1 surface, which consists of rows of dimers, provides the possibility for the silicon dimer to act as a dienophile in a Diels–Alder [4 + 2] cycloaddition reaction. These dimers are formed by a σ -bond and a π -like interaction,¹¹ in analogy to a C=C double bond, although we note that most experimental studies of clean Si(100) show the dimers to be buckled and not entirely covalent.¹² The Diels–Alder reaction leading to a Si₂C₄ adduct is documented to occur in solution,¹³ and Diels–Alder adducts in other large geometry systems such as W₂ and Mo₂ dimers^{14,15} or silica¹⁶ have been proposed. Theoretical predictions by Konecny and Doren⁸ show that, on the silicon surface, [4 + 2] cycloaddition should occur at room temperature without significant barrier and lead to the formation of a stable adduct.

On the Si(100)-2×1 surface, another possible reaction pathway is interaction of only one double bond with the Si dimer atoms. The resulting [2 + 2] reaction, referred to as di- σ -bonding, has been proposed to explain adsorption of alkenes and alkynes, which react with high probability on Si(100)-2×1.^{3–7} For a multiply π -bonded molecule such as a diene, [2 + 2] bonding would result in one C=C double bond left unreacted with the surface. Konecny and Doren have calculated

for 1,3-cyclohexadiene that the [2 + 2] reaction product is 15 kcal/mol less thermodynamically stable than the [4 + 2] Diels–Alder adduct, primarily due to bond strain.⁸ A similar result is expected for butadienes.

In this paper we present evidence for the formation of a Diels–Alder adduct on the Si(100)-2×1 surface, which is based upon the vibrational spectra of dienes chemisorbed on this surface at room temperature. In Figure 1, the products of the reaction of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene with a silicon dimer by either Diels–Alder cycloaddition or [2 + 2] addition are illustrated schematically. It is clear from the figure that the resulting structures differ significantly and present the opportunity for identification by vibrational spectroscopy.

The studies presented here were performed in an ultrahigh vacuum chamber described in detail elsewhere.¹⁷ The IR data were collected in a multiple internal reflection mode using unpolarized light at 4 cm⁻¹ resolution. The sample was cleaned by sputtering with Ar⁺ ions at room temperature and annealing at 1050 K for 25 min. Subsequently, the sample was exposed to Si₂H₆ while cooling from 870 to 600 K in order to prepare a smooth Si(100)-2×1 surface. The quality of the surface was confirmed by the presence of sharp monohydride features in the IR spectra prior to flashing the hydrogen off at 900 K. Freeze–pump–thaw cycles were used for purification of liquid hydrocarbons. Gaseous hydrocarbons were used without further purification. The purity of the compounds was verified *in situ* by mass spectrometry. The sample of *cis*-polybutadiene (Aldrich) was obtained by depositing polybutadiene dissolved in CCl₄ onto a KBr substrate and allowing the solvent to evaporate.

Figure 2 shows infrared spectra of 1,3-butadiene chemisorbed on Si(100)-2×1 at room temperature and physisorbed at low temperature. Separate measurements indicate that butadiene does not dissociate at either temperature.¹⁸ Because IR studies as a function of coverage showed changes in the spectra at high exposures (≥ 10 L), the room temperature exposures in Figure 2 were kept at or below 1 L to avoid the possibility of intermolecular interactions. Auger electron spectroscopy (AES) measurements in another vacuum system verified that 1 L exposure generates subsaturation coverage. Also shown in Figure 2 for comparison are spectra of 1,3-butadiene-1,1,4,4-*d*₄ (CD₂=CH–CH=CD₂), polybutadiene ($\{-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\}_n$), and multilayers of 1,3-butadiene.

The spectrum of chemisorbed butadiene shows absorption features at 2994 and near 2895 cm⁻¹. The assignment of the infrared spectrum of chemisorbed butadiene is facilitated by the butadiene-*d*₄ studies. The spectrum of the deuterated compound chemisorbed at room temperature exhibits only one C–H stretch, at 2989 cm⁻¹; the C–D stretches were too weak to be observed. The C–H mode must correspond to hydrogen atoms bonded to the carbon atoms in the β - and γ -positions, and the mode near 2895 cm⁻¹ observed for the nondeuterated compound therefore is assigned to the CH₂ groups. Clearly absent from the chemisorbed butadiene spectrum is any mode at higher wavenumber (~ 3080 cm⁻¹) corresponding to the terminal =CH₂ stretch. In contrast, this vinylic CH stretch is one of the strongest modes in the molecular (multilayer) spectrum.

The spectrum observed following chemisorption of butadiene is inconsistent with the [2 + 2] bonded adduct (Figure 1a), which would be expected to show a distinctive signature of the terminal =CH₂ modes. Instead, the CH₂ groups in the chemisorption adduct lead to a broad absorption near 2895 cm⁻¹, which are close to the stretching frequencies observed for CH₂ modes in many alkanes.^{19,20} Although the assignment of this feature is tentative, we suggest that the symmetric and asym-

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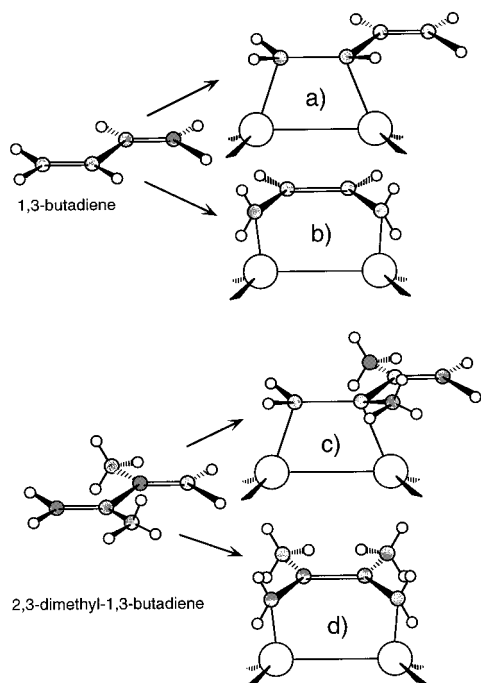


Figure 1. Possible adducts of the reaction of butadienes with the Si(100)-2 \times 1 surface.

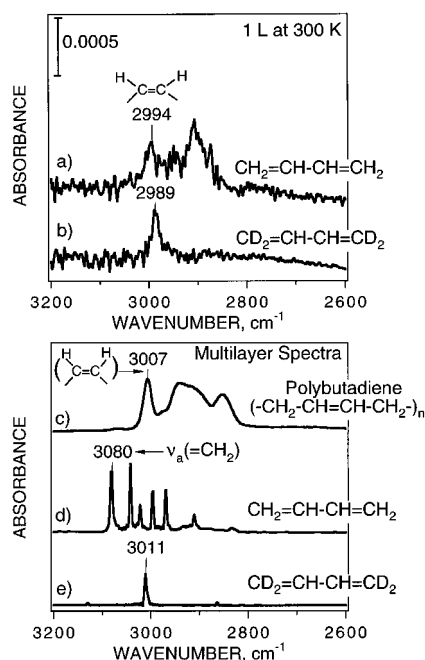


Figure 2. Infrared spectra of 1,3-butadiene adsorbed on a Si(100)-2 \times 1 surface: (a) 1 L of 1,3-butadiene adsorbed at 300 K; (b) 1 L of 1,3-butadiene-1,1,4,4- d_4 adsorbed at 300 K; (c) polybutadiene; (d) multilayers of 1,3-butadiene (1000 L) at 100 K; (e) multilayers of 1,3-butadiene-1,1,4,4- d_4 (1000 L) at 100 K.

metric CH_2 modes usually at 2850 and 2920 cm^{-1} are unresolved in the spectrum and are seen as a broad peak centered at 2895 cm^{-1} . We note that Hamers *et al.* observed a similar stretching frequency for the CH_2 at the apex of cyclopentene chemisorbed on silicon.²¹ Furthermore, the mode near 2990 cm^{-1} is consistent with the vibrations of C-H in the α -position with respect to an internal double bond. This assignment is confirmed by comparison to the spectrum of polybutadiene, which shows a similar feature near 3007 cm^{-1} . The spectrum obtained for chemisorbed butadiene is in closest agreement with

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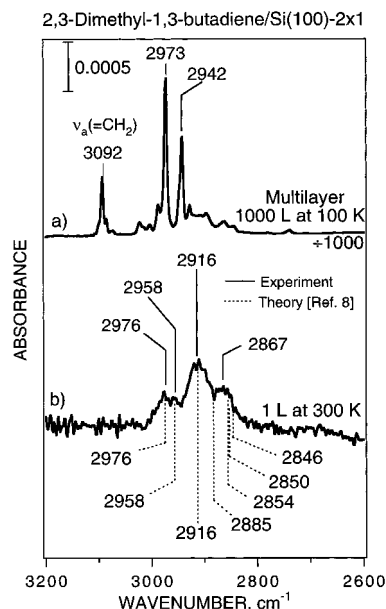


Figure 3. Infrared spectra of 2,3-dimethyl-1,3-butadiene adsorbed on a Si(100)-2 \times 1 surface: (a) multilayers at 100 K; (b) 1 L at 300 K.

the structure shown in Figure 1b, which corresponds to the Diels-Alder adduct.

In order to confirm the spectroscopic assignment of the formation of a Diels-Alder adduct in the reaction of dienes with a Si(100)-2 \times 1 surface, 2,3-dimethyl-1,3-butadiene was also studied. Figure 1 shows that if this compound undergoes [2 + 2] addition (Figure 1c), it will still contain two vinylic protons, while the Diels-Alder adduct (Figure 1d) will contain none. As for butadiene, these particular protons can be easily distinguished from the other vibrational signatures. In Figure 3, multilayers of 2,3-dimethyl-1,3-butadiene condensed on a surface at 100 K show a sharp, intense feature at 3092 cm^{-1} ($\nu_a(\text{=CH}_2)$); when the spectrum is collected at room temperature, this feature is absent. Only modes corresponding to $-\text{CH}_2-$ and $-\text{CH}_3$ vibrations remain. By comparison with cyclohexenes and other cyclic compounds,^{21,22} the peaks at 2916 cm^{-1} and near 2850 cm^{-1} are assigned to CH_2 ring modes, and the features at 2976 and 2958 cm^{-1} are assigned to the asymmetric methyl stretch.

To help confirm the assignment of the spectrum following chemisorption of 2,3-dimethyl-1,3-butadiene, vibrational frequencies for the Diels-Alder adduct calculated by Konecny and Doren⁸ are shown in Figure 3. The calculated frequencies have been scaled by 0.94 for the best agreement with experiment. Similar scaling factors are typically used in such vibrational frequency calculations.²³ It is evident from Figure 3 that the agreement between the experiment and theory is excellent. The results strongly support the conclusion that the Diels-Alder adduct is formed on a Si(100)-2 \times 1 surface upon chemisorption of 2,3-dimethyl-1,3-butadiene.

In conclusion, the infrared spectra taken following chemisorption of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene on Si(100)-2 \times 1 give evidence for the formation of a Diels-Alder adduct. Agreement between experiment and theory is excellent. To our knowledge, this is the first example of a Diels-Alder cycloaddition reaction occurring on a single-crystalline silicon surface, with the Si dimer atoms acting as a dienophile.

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