

## Stereoselectivity in Molecule–Surface Reactions: Adsorption of Ethylene on the Silicon(001) Surface

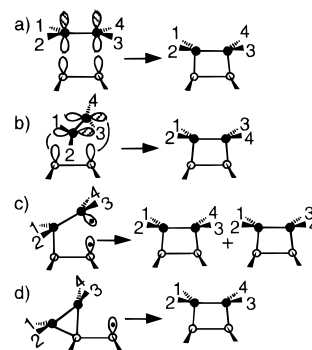
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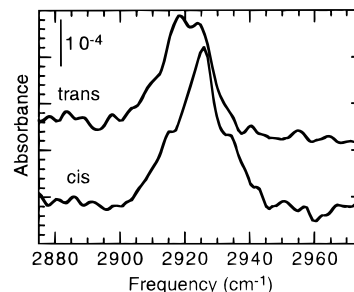
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The reactions of unsaturated organic compounds are often intimately connected with the symmetry properties of the frontier orbitals of the reactants and products.<sup>1,2</sup> These symmetry-based rules have been applied successfully to a wide variety of organic reactions, such as addition reactions of alkenes and dienes. The (001) surface of silicon is comprised of silicon atoms paired together into dimers, forming a (2 × 1) reconstruction. The frontier orbitals of these dimers are  $\pi$  bonding and  $\pi^*$  anti-bonding orbitals analogous to those of alkenes, suggesting that the Si=Si bonds of the Si(001) surface and the C=C bonds of alkenes may share some similarities in reaction mechanisms.<sup>3,4</sup> Alkenes and alkynes react with high probability with Si(001) by cleaving the Si=Si and C=C  $\pi$  bonds to form two new Si–C  $\sigma$  bonds.<sup>5–13</sup> At low coverages, ethylene molecules adsorb on top of every second Si=Si dimer; once this structure is completely filled, adsorption continues to fill in the remaining Si=Si dimer sites.<sup>6,7,11</sup> Cyclopentene and other unsaturated organics can also form ordered layers by bonding to the Si=Si dimers.<sup>13</sup> While addition reactions between alkenes and the Si(001) dimers are generally facile, almost nothing is known about the stereochemistry or mechanisms of these reactions. In this communication, we show that these reactions occur in a highly stereospecific way, and we relate this to several possible mechanisms for concerted and nonconcerted reactions.

According to the Woodward–Hoffmann rules, a concerted suprafacial reaction between ethylene and a Si(001) dimer (a  $[2\pi_s + 2\pi_s]$  cycloaddition), as in Figure 1a, is symmetry-forbidden.<sup>1</sup> The antarafacial + suprafacial,  $[2\pi_a + 2\pi_s]$ , reaction in Figure 1b is symmetry-allowed but is sterically hindered; in this case the C–C bond must twist during the reaction, so that the stereochemistry of the final product is inverted. Alternatively, it is possible to have a two-step process in which the  $\pi$  bonds of the surface dimers and the ethylene molecule are broken first to form a diradical intermediate as in Figure 1c, followed by formation of a second Si–C bond. In this case



**Figure 1.** Possible models for adsorption of ethylene on the Si(001) surface, as discussed in the text.



**Figure 2.** P-polarized absorption spectra for *cis*- and *trans*-1,2-dideuterioethylene on the two-domain Si(001) surface.

once the ethylene  $\pi$  bond is broken rotation around the C–C bond is possible, causing loss of stereoselectivity if it occurs before the second Si–C bond is formed. Recently a three-atom intermediate has been proposed for acetylene on Si(001).<sup>14,15</sup> A similar intermediate for ethylene could be formed as in Figure 1d; in this case stereochemistry should be retained as the alkene slides in to the Si–Si dimer bond. For the mechanisms in Figure 1, we find that mechanism 1b inverts the symmetry, mechanisms 1a and 1d retain the stereochemistry of the reactant, and mechanism 1c scrambles the symmetry.

To investigate the stereochemistry experimentally, we have utilized Fourier-transform infrared (FTIR) spectroscopy on surfaces exposed to *trans*- and *cis*-1,2-dideuterioethylene. These experiments were conducted under ultrahigh vacuum conditions using a multiple internal reflection geometry, as described previously, with 2  $\text{cm}^{-1}$  resolution.<sup>16</sup> Because the bonding of ethylene changes at high coverage, the spectra shown here were obtained at coverages of less than 0.2 monolayer, although a range of coverages was explored. Two types of samples were used: “On-axis” Si(001) samples contain a mixture of two equivalent domains of dimer orientations, rotated by 90° with respect to one another. “Off-axis”, or “vicinal”, Si(001) samples are miscut off (001) by 4° toward the  $\langle 1\bar{1}0 \rangle$  direction; on these samples the dimers are all oriented in the same direction across the entire sample, thereby permitting polarized FTIR spectra to probe infrared transition dipole components along different dimer orientations.<sup>13,17</sup>

Figure 2 shows infrared spectra obtained using p-polarized light and “on-axis” samples for *cis*- and *trans*-1,2-dideuterioethylene. The differences between these IR spectra demonstrate that the chemisorption of ethylene on Si(001) occurs in a stereoselective manner. To identify the stereochemistry of the products, we use infrared spectroscopy on single-domain

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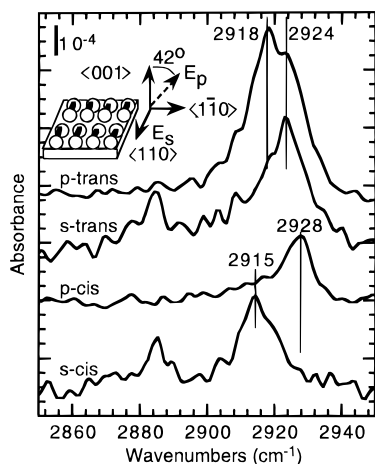
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**Figure 3.** s- and p-polarized absorption spectra for *cis*- and *trans*-1,2-dideuterioethylene on the single-domain Si(001) surface. The inset shows the electric field vectors of the incident light in relation to the Si(001) dimers and the crystallographic directions of the sample.

**Table 1.** Observed Frequencies and Polarizations for *cis*- and *trans*-1,2-Dideuterioethylene on Si(001)

reactant symmetry	frequency (cm <sup>-1</sup> )	polarizn	C-H mode	splitting (cm <sup>-1</sup> )
<i>cis</i>	2915	s	as	13
	2928	p	s	
<i>trans</i>	2918	p	s	6
	2924	s, p	as	

(vicinal) Si(001) samples. In the chosen geometry s-polarized light has its electric field vector parallel to the Si=Si dimer bonds, while the p-polarized light has a component normal to the surface and a component in the surface plane perpendicular to the Si=Si dimer bond as indicated in Figure 3. Figure 3 shows spectra for *cis*- and *trans*-1,2-dideuterioethylene on Si(001) with s- and p-polarized light, while Table 1 summarizes the frequencies and symmetry (asymmetric (as) and symmetric (s)) of the modes on the basis of our polarization measurements. Note that the splitting between asymmetric and symmetric modes when using the *cis*-reactant is 13 cm<sup>-1</sup>, while when using the *trans*-reactant it is only 6 cm<sup>-1</sup>. The small peak near 2885 cm<sup>-1</sup> in Figure 3 is an isotopic impurity of nondeuterated ethylene.

To help determine the geometry of the *cis*- and *trans*-ethylenes after adsorption on Si(001), we have calculated the vibrational frequencies for the (*R,S*) and (*R,R*) products on a nine-atom Si cluster using the Gaussian 94 *ab initio* program, using the 6-31+G\* basis set and the Becke3LYP density functional.<sup>16,18</sup> The (*R,S*) and (*S,R*) diastereomers are equivalent and have the two C-H bonds on the same side of the C-C bond in a *cis*-like configuration; the (*R,R*) and (*S,S*) forms are equivalent

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**Table 2.** Calculated Frequencies and Polarizations for *cis*- and *trans*-1,2-Dideuterioethylene on Si(001)

product geometry	frequency (cm <sup>-1</sup> )	frequency × 0.948 (cm <sup>-1</sup> )	polarizn	C-H mode	splitting (cm <sup>-1</sup> )
( <i>RS</i> ), ( <i>SR</i> )	3073	2913	s	as	15
( <i>cis</i> -like)	3089	2928	p	s	
( <i>RR</i> ), ( <i>SS</i> )	3078	2918	p	s	6
( <i>trans</i> -like)	3084	2924	s, p	as	

and have the two C-H bonds on opposite sides of the C-C bond in a *trans*-like configuration. Table 2 gives the calculated frequencies, mode symmetry, and incident polarization required for observation according to our experimental geometry; also shown are frequencies after scaling by 0.948 to correct for systematic errors in the frequency calculations.<sup>19</sup> Our calculations predict a splitting of 15 cm<sup>-1</sup> for the (*RS*) *cis*-like configuration but only 6 cm<sup>-1</sup> for the (*RR*) *trans*-like configuration.

A comparison of the data in Tables 1 and Table 2 shows that they are in excellent agreement. The results show that the symmetry of the original reactant is retained, so that *cis*-1,2-dideuterioethylene adsorbs to form an (*R,S*) or (*S,R*) product, and the *trans*-1,2-dideuterioethylene adsorbs to form an (*R,R*) or equivalent (*S,S*) product.

Our results suggest that reaction does not proceed via the "allowed" [2 $\pi_a$  + 2 $\pi_s$ ] mechanism (Figure 1b), as this predicts the incorrect stereochemistry. However, violations of the Woodward-Hoffmann rules might be expected for silicon compounds due to the much smaller separation of the  $\pi$  and  $\pi^*$  frontier orbitals in Si=Si dimers than in alkenes.<sup>14</sup> Additionally, there is some previous evidence for cleavage of the Si-Si  $\sigma$  bond upon ethylene adsorption,<sup>9,10</sup> although this remains controversial.<sup>12</sup> The diradical mechanism shown in Figure 1c could account for our observations only if rotation about the C-C single bond (which would scramble the stereochemistry) does not occur, due to rapid formation of a second Si-C bond or to possible hindrance of bond rotation by the surface. Finally, a mechanism involving the three-center intermediate shown in Figure 1d could also account for the observed stereochemistry if there is a smooth progression toward the final product without C-C bond rotation. These results suggest that the addition reactions of ethylene on Si(001) probably do not involve a concerted reaction mechanism, but more likely involve a low-symmetry but short-lived intermediate such as those shown in Figure 1c,d. The weakness of the Si=Si dimer  $\pi$  bond should make formation of radical-like intermediates such as those shown in Figure 1c,d more likely on Si(001) surfaces than on analogous alkenes. Indeed, previous results on disilenes show a similar propensity toward diradical mechanisms.<sup>4</sup>

The strong differences in infrared spectra obtained from the *cis*- and *trans*-reactants demonstrate that the interaction of ethylene with the Si(001) is stereospecific and almost totally stereoselective. To the best of our knowledge, this is the first report of a stereochemically selective reaction occurring on a solid surface with no intrinsic chirality.

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