The reaction of tetrahydrofuran (THF), an otherwise inert solvent molecule, on Si(001) was experimentally studied in ultrahigh vacuum. Using scanning tunneling microscopy (STM) and photoelectron spectroscopy at variable temperature, we could both isolate a dative bound intermediate state of THF on Si(001), as well as the final configuration that bridges two dimer rows of the Si(001) surface after ether cleavage. The latter configuration implies splitting of the O–C bond, which is typically kinetically suppressed. THF thus exhibits a hitherto unknown reactivity on Si(001).

The (001) surface of silicon is the basis of most semiconductor devices, and its functionalization with organic molecules is seen as a possibility for further miniaturization when conventional semiconductor device technology will have reached its physical limit. Thus, organic chemistry on Si(001) is of particular importance. The clean Si(001) surface is characterized by the formation of rows of buckled dimers with one doubly occupied and one empty dangling bond at the upper and lower Si atoms, respectively (Figure 1). Reactions of smaller organic molecules typically occur on one single dimer, most prominent are [2+2] cycloadditions (1→2 in Figure 1a), which are symmetry-forbidden as a concerted process but can proceed on the surface via an asymmetric intermediate and thus with high reactivity. Numerous organic compounds containing π bonds, such as alkenes, alkynes, and azides have been investigated.

The second major reaction mechanism can be described as a polar dissociative addition, for example, alcohols add to the silicon dimer via splitting the O–H bond and forming new Si–H and Si–O bonds (1→3 in Figure 1a). Primary and secondary amines react via an analog reaction channel. The polar dissociative addition stresses the zwitterionic character of the Si dimer depicted in Figure 1b: the reaction includes an intermediate state involving a dative bond between the lone pair of, for example, the nitrogen atom of an amine and the positively charged lower silicon atom. Here we show that this reaction channel even enables the cleavage of the O–C bond of an ether group which is known for its low reactivity and is thus used as stable backbond unit in larger molecules or in solvent molecules, such as THF (4 in Figure 1a).

A typical STM image as obtained after adsorption of a small amount of THF at a low surface temperature (LT, T=50 K) is shown in Figure 2a. One observes grey elliptical signatures with their longer semiaxis parallel to the dimer rows. Their darker surroundings disrupt the well-observable zig-zag structure of the Si(001) c(4×2) surface reconstruction. Furthermore, from comparison with the c(4×2) structure of the substrate, one can deduce that the configurations are always located at the lower atom of the Si dimer (Figures 2b,c). A different adsorption geometry is observed in the room-temperature (RT) STM images (Figure 3). In clear distinction to the LT configuration, it involves two Si dimers of neighboring dimer rows and leads to two bright spots on the outer dimer atoms of the involved dimers as shown in the detailed images in Figures 3a,b. These features are considerably brighter in empty-state STM images (Figures 3a,c); they are separated by
adsorbed at T \approx 50 K. An enlargement of the marked area is shown in (b). A single, site-specific adsorption geometry is observed, the white arrows indicate the orientation of the next-neighbor dimers on the opposite dimer row with the arrowhead pointing to the lower Si atom (yellow circles). One LT adsorption geometry is marked in (b) by a blue ellipse. c) Ball-and-stick model (top view) of the Si(001) surface with THF molecule adsorbed.

Figure 2. a) Empty-state STM image (30×30 nm², +0.8 V, 0.3 nA) of Si(001) covered by 0.02 monolayer (ML, 1 ML = 1 THF molecule per Si-dimer) THF adsorbed at T \approx 50 K. An enlargement of the marked area is shown in (b). b) A single, site-specific adsorption geometry is observed, the white arrows indicate the orientation of the next-neighbor dimers on the opposite dimer row with the arrowhead pointing to the lower Si atom (yellow circles). One LT adsorption geometry is marked in (b) by a blue ellipse. c) Ball-and-stick model (top view) of the Si(001) surface with THF molecule adsorbed.

d) Sketch of the RT adsorption geometry is concluded. This linear configuration can bridge two Si dimer rows, as observed in the STM images (Figure 3).

Detailed information on the electronic structure of the different bonding configurations, especially with respect to the valence orbitals, is obtained from ultraviolet photoelectron spectroscopy (UPS) measurements. Figures 4a,b show the O 1s and C 1s spectra of a submonolayer THF on Si(001), respectively. The O 1s spectra indicate a phase transition from the LT phase (binding energy E_B LT = 535.0 eV, blue) to the RT phase (E_B RT = 532.2 eV, red) by an energetic shift of \Delta E_B = 2.8 eV to lower binding energies. The O 1s binding energy as obtained from a multilayer of THF is E_B mult = 534.4 eV (Figure 2a in the Supporting Information). The higher binding energy of the O 1s electron of the submonolayer configuration when compared to the multilayer indicates a lower valence electron density at the oxygen atom in the LT submonolayer configuration. In combination with the site-selective adsorption of the THF molecule at the lower atom of the Si dimer at low temperature (Figure 2), an electron donation into the empty D down orbital, that is, a dative bonding situation, can be concluded. Such a dative bonding leaves the THF molecule intact. As a consequence we find the C–C–C and C–C–O lines in the C 1s spectrum measured at 50 K to be of the same intensity (Figure 4b) in accordance with the symmetric structure of the THF molecule.

The shift of the O 1s peak to lower binding energies at RT is attributed to a covalently attached oxygen atom to the Si(001) surface due to the lower electronegativity of Si when compared to C. \(^{11,14}\) This observation requires the breaking of a O–C bond and the concomitant ring opening of the THF molecule. In parallel to the change of the O 1s peak, the C 1s RT spectrum cannot be described with only two peaks anymore but three peaks are identified. If we take into account the electronegativity \(\gamma\) of the elements under inspection with \(\gamma_D > \gamma_C > \gamma_Si\) these three peaks are attributed to C atoms in C–C–O (highest binding energy), C–C–C (middle peak), and C–C–Si (lowest binding energy) configurations according to an increase in electron density at the corresponding C atom. From the intensity ratio C–C–O:C–C–C:C–C–Si = 1:1.9:0.8 a Si–O–(CH\(_2\))\(_x\)–Si adsorption geometry is concluded. This linear configuration can bridge two Si dimer rows, as observed in the STM images (Figure 3).

Figure 3. STM images (6×6 nm²) of Si(001) after the adsorption of 0.02 ML THF at T = 300 K at a) positive sample bias (+0.8 V, 0.5 nA) and b) negative sample bias (−2.0 V, 0.5 nA). A single adsorption geometry, involving two Si dimers of neighboring dimer rows, is observed. c) STM image (20×20 nm², +1.2 V, 0.25 nA) at 0.04 ML THF coverage. d) Sketch of the RT adsorption configurations across the dimer rows (black), associated dangling-bond configurations (white) and unreacted Si dimers (yellow), for easier inspection the dimers are drawn in symmetric configuration. Solid ellipses in (c) indicate adsorption sites of a single THF molecule, dotted and dashed ellipses indicate adsorption of two or three THF molecules in a row perpendicular to the dimer rows, respectively.

a dark center between the dimer rows. From the dependence of their appearance on sample bias, the bright spots are interpreted as single dangling-bond configurations\(^{11,12}\) and accordingly the dark center as the actual THF configuration at room temperature. This interpretation is further backed by STM images taken at a slightly higher THF coverage (Figure 3c). In addition to the configurations that bridge two dimer rows, one also observes configurations across three and four dimer rows with bright spots only at the outer dimer atoms. These configurations can be explained by the successive adsorption of a further THF molecule at one of the two single dangling-bond configurations of an already adsorbed molecule. This leads then to the suppression of one of the original bright spots and the formation of an additional single dangling bond shifted by one dimer row (Figure 3d). The observed RT configurations thus require two covalent bonds between the reacted former THF molecule and the inner atoms of the involved Si dimers of two neighboring dimer rows.\(^{13}\)
The energy scale of these spectra is calibrated by the He-II spectrum of the clean Si(001) surface, which shows a clearly resolved signal of the D$_{up}$ orbital, labelled (I) in Figure 4c. The multilayer spectrum is comparable to the gas-phase spectrum of THF, indicating an intact molecule. Interestingly, the UPS spectrum of a submonolayer at 50 K is almost identical to the multilayer spectrum except for a reduced intensity at peak (II), which is attributed to the highest occupied molecular orbital (HOMO) and has a large contribution from the electron lone pairs of the oxygen atom. This indicates a reaction involving the oxygen lone pair thus further backing the interpretation of a dative bonding at low temperatures.

On the other hand, the UPS spectrum at 300 K is completely different from the LT spectrum. Specifically, some well-defined peaks of the multilayer spectrum have disappeared. The arrow labelled (IV) highlights the binding energy of a molecular orbital associated with the circular structure of the THF molecule. The absent electron density at this energy at RT is consistent with a ring-opening reaction. On the other hand, the peak structure (III), which is assigned to C/C and C/H bonds, is almost unaffected when comparing the LT and RT spectra.

Thus, our investigations clearly show that the reaction pathway of THF on Si(001) proceeds via a datively bonded intermediate to a Si–O–(CH$_2$)$_n$–Si adsorption geometry bridging two Si atoms of neighboring dimer rows. These findings are furthermore backed by DFT calculations, which identify both the datively bonded intermediate as well as the final configuration bridging two dimer rows as local minima of this potential energy surface. Calculated STM images based on these results, which are shown in Figures 5b,c, compare well to the experimental results.

To the best of our knowledge, a datively bonded species involving an oxygen atom as electron donor on Si(001) has not been observed experimentally before. While dative bonds via a nitrogen atom, such as those of tertiary amines, are well known on Si(001), experimental results on dative bonds via an oxygen atom on group IV semiconductors have been reported only on germanium, for example, for diethyl ether on Ge(001). This might be surprising at first glance, since one expects a higher binding energy for the Si–O dative bond when compared to Ge–O due to the higher electron affinity of Si. However, it can be explained by the fact that, in the case of previous experiments on Si(001), the Si–O dative bond was too short-lived because the following reaction steps, such as the O–H cleavage of the hydroxyl group, were much faster than O–C cleavage.
Indeed, from experiments on diethyl ether on Ge(001), for which no dissociation has been observed, one might conclude that the ether bond is rather inert also with respect to group IV semiconductor surfaces. However, our results draw a very different picture. We do not only observe a cleavage of the ether bond, but a reaction pathway that leads to the bridging of two dimer rows, an otherwise very rare reaction channel. So how can we explain this unexpected reaction pathway?

From solution chemistry, it is known that cleavage of the O–C bond in THF can be promoted via an initial complexation of the oxygen atom by an electron-pair acceptor that lowers the antibonding O–C σ* orbital. Filling electrons into this otherwise empty antibonding orbital results in O–C bond cleavage. In the case of THF cleavage on Si(001), the unfilled dangling bond at the lower Si atom acts as electron-pair acceptor, as confirmed by the observation of the dative bond formation at the D_down orbital. In further analogy, one can imagine that filled D_up states then act as the corresponding electron donors. On the static c(4×2) reconstruction of Si(001) (Figure 1c), they are accessible on neighboring dimers of the same dimer row. Thermally activated flipping of the dimers at elevated temperatures can also provide a filled dangling bond at the neighboring Si atom of the opposite dimer row, the Si atom that is the binding site of the final configuration.

In summary, we were able to isolate a datively bonded oxygen species on Si(001) which is discussed as an important intermediate state for many surface reactions on Si(001) such as adsorption of alcohols or carbonyls. We furthermore observed the otherwise kinetically suppressed dissociation of the O–C bond of the ether group. In the case of THF/Si(001), this leads to a final configuration that bridges two dimer rows.

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Keywords: ether cleavage · silicon surface · STM · tetrahydrofuran · XPS

[13] Once the RT configuration is formed, either by heating the surface to or adsorption at RT, it is also stable at low temperatures.
[18] Calculations based on B3LYP/6-31G*.
[19] The calculated images do not take into account the thermally activated flipping of the buckled Si dimers at room temperature. As a consequence, the calculated final configuration does not appear symmetric, in contrast to the STM images taken at room temperature.