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Ethers on Si(001): A prime example for the common ground between surface science and molecular organic chemistry
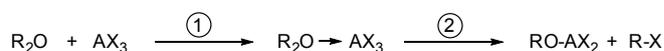
Lisa Pecher, Slimane Laref,† Marc Raupach and Ralf Tonner*

Abstract: Using computational chemistry, we show that the adsorption of ether molecules on Si(001) under ultra-high vacuum conditions can be understood with textbook organic chemistry. The two-step reaction mechanism of (1) dative bond formation between the ether oxygen and a Lewis acidic surface atom and (2) a nucleophilic attack of a nearby Lewis basic surface atom is analysed in detail and found to mirror the acid-catalysed ether cleavage in solution. The O-Si dative bond is found to be the strongest of its kind and reactivity from this state defies the Bell-Evans-Polanyi principle. Electron rearrangement during the C-O bond cleavage is visualized using a newly developed bonding analysis method, which shows that the mechanism of nucleophilic substitutions on semiconductor surfaces is identical to molecular chemistry S_N2 reactions. Our findings thus illustrate how the fields of surface science and molecular chemistry can mutually benefit and unexpected insight can be gained.

In the last decades, material science and surface science have become research fields of ongoing importance pushing forward the development of new technologies and electronic devices. More recently, organic molecules began to be used, e.g. in the construction of organic light-emitting devices (OLED)[1] or the organic functionalization of semiconductors.[2] Chemical expertise is indispensable in describing bonding and reactivity phenomena in these fields.[3] Especially on semiconductor surfaces, where electronic states are more localized compared to delocalized states on metals, the surface often behaves like a molecular reagent and solution chemistry concepts can be very helpful in describing the system.[4]
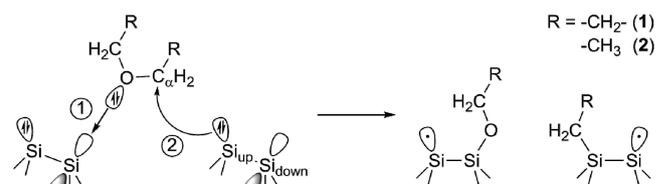
The understanding and prediction of molecular reactivity has highly benefitted from the use of computational methods analyzing the chemical bond (See e.g. Ref. [5] for an overview). Many of these methods have been successfully transferred and applied to periodic systems, including (but not limited to) the Crystal Overlap Hamilton Population (COHP),[6] the Electron Localization Index (ELI),[7] Energy Decomposition Analysis (EDA),[8] Natural Bond Orbital (NBO) Analysis[9] and the Quantum Theory of Atoms In Molecules (QTAIM).[10] By applying bonding analysis methods to the prime example of ether molecules on

Si(001), we will highlight the ability of molecular organic chemistry to help in understanding surface science.

The Si(001) surface is a widely used substrate due to its relevance for application[11] and its high reactivity arising from both a nucleophilic and electrophilic character of individual surface atoms.[12] Ethers show an unexpectedly rich reactivity on this surface, a result that sparked extensive experimental investigations.[13] These were able to spectroscopically prove a datively bonded (DB) intermediate and subsequent regioselective C-O bond breaking with a sizeable barrier. The surface-induced bond cleavage was proposed to stem from ω^*(C-O) occupation in the DB state facilitated by surface dimer flipping.[13a] These results render the system an ideal model for our theoretical approach. In molecular chemistry, C-O bond cleavage is known to occur in several ways. One of the most prominent examples (Scheme 1) is ether activation by a strong Lewis acid[14] (e.g. $AX_3 = AlCl_3$) followed by a nucleophilic attack at C_ζ.[15]

[a] Lisa Pecher, Dr. Slimane Laref, Dr. Marc Raupach,
     PD Dr. Ralf Tonner
     Faculty of Chemistry and Material Sciences Center
     Philipps-Universität Marburg
     Hans-Meerwein-Str. 4, 35032 Marburg, Germany
     E-mail: tonner@chemie.uni-marburg.de

†   Current address: King Abdullah University of Science and
     Technology (KAUST), Physical Science and Engineering Division
     (PSE), Thuwal 23955, Saudi Arabia

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     the document.

Scheme 1. Ether cleavage via Lewis acid (AX_3) activation and subsequent bond breaking.

Scheme 2. Two-step reaction of ether molecules with the Si(001) surface: (1) Dative bond formation between the ether oxygen and a Si_{down} surface atom via donation into the empty p orbital; (2) Nucleophilic attack of a nearby Si_{up} atom at C_ζ. Dots indicate unpaired electrons (dangling bonds).
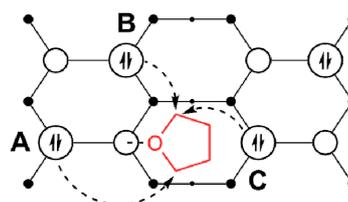
Scheme 3 Nucleophilic Si_{up} atoms **A**, **B** and **C** are close enough to initiate an attack at C_ζ of adsorbed tetrahydrofuran (**1**) (Scheme 2, step 2). The products will be denoted as A, B and C. Diethylether (**2**) shows the same reactivity.[16]

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The well-known surface reconstruction of Si(001) sees the formation of buckled dimers with an electronic structure well approximated by an empty p orbital at the Lewis acidic Si_{down} dimer atom and a non-bonding electron pair at the Lewis basic and nucleophilic Si_{up} atom (Scheme 2).[12] Therefore, a mechanism analogous to the molecular reaction outlined above suggests itself: In the first step, a DB intermediate is formed between the oxygen and Si_{down} atoms while in the second step, any nearby nucleophilic Si_{up} atom can attack a C_α atom to form a covalent Si-C bond (Scheme 2).[13a] This type of reaction has been reported in recent years for haloalkanes and other types of molecules on semiconductor surfaces[17] and was also deduced from the experimental investigations on surface reactivity of ethers on Si(001).[13] Regioselectivity is another important aspect, since there are three Si_{up} atoms close enough to initiate the nucleophilic attack (Scheme 3) but only reaction via atom **C** is observed in experiment.[13a] Applying molecular chemistry concepts, one would expect the main product to occur for the reaction which is able to establish a transition state (TS) structure most closely to the trigonal bipyramidal structure of S_N2 reactions in gas phase and solution.[18] We will now apply computational analysis methods to the example of tetrahydrofuran (**1**) on Si(001) to verify that the reaction mechanism is identical to a molecular chemistry S_N2 reaction and furthermore gain a quantitative insight into bonding and reactivity. The findings for **1** are confirmed by equivalent investigations of diethylether (**2**), which rules out ring

strain as the determining factor and shows that the results are more general for the compound class of ethers (see Supporting Information) - in line with the conclusions from the experimental investigations.[13]

The bond between the ether oxygen atom and the surface in the DB intermediate (Scheme 2, step 1) can be analyzed using our recently developed periodic EDA (pEDA).[8a] The pEDA allows to decompose the interaction energy $\div E_{int}$ into dispersion and electronic effects and the latter part additionally into well-defined contributions from Pauli repulsion, electrostatics and orbital interaction.[19] The results (Table 1) show that electronic effects make up the majority (67%) of the interaction energy, underlining that this structure can be understood as being chemisorbed.[8b] Furthermore, electrostatic interaction dominates the attractive terms of the electronic interaction energy at 55% (orbital interaction: 45%). Such an outweighing of electrostatics in covalently bound systems has been shown to be a typical feature of a dative bond.[20] The orbital term can further be decomposed using the Natural Orbitals for Chemical Valence (NOCV) scheme[21] and the charge redistribution of the individual contributions visualized as deformation densities $\div \psi_i$. Visual inspection then allows to distinguish between different types of chemical bonding (e.g. ω/ϕ, donation/back donation). The largest contribution for this system (Figure 1a) mainly shows charge flow from a p orbital shaped electron density at the oxygen atom (red lobes) into the bonding region between the O and Si_{down} atoms (blue lobes),[22] another typical feature of a dative bond.[8b,23]

Table 1. Bonding analysis (pEDA) of the molecule-surface interaction between **1** and Si(001) for the dative bond (DB) intermediate and the transition state (TS) of the reaction from the DB intermediate to product C (see also Schemes 2 and 3).[a]

	DB intermediate (1)		TS(DB→C) (2)	
$\div E_{int}$	−156		−235	
$\div E_{int}(disp)$[b]‡	−51	(33%)	−52	(22%)
$\div E_{int}(elec)$[b]‡	−105	(67%)	−183	(78%)
$\div E_{Pauli}$	656		979	
$\div E_{elstat}$[c]	−417	(55%)	−600	(52%)
$\div E_{orb}$[c]	−344	(45%)	−562	(48%)
$\div E_{orb}(dative)$[d]	−293	(85%)	−397	(71%)
$\div E_{orb}(S_N)$[d]	0		−111	(20%)
$\div E_{prep}$	22		157	
E_{bond}[e]	−134	(−132)	−78	(−79)

[a] All values in kJ mol^{-1}, calculated using PBE-D3/TZ2P. Fragments used are molecule and surface. Ground state (1) and transition state (TS) (2) structure analyzed. [b] Percentage values: Relative contributions of dispersion and electronic effects to the interaction energy $\div E_{int}$. [c] Percentage values: Relative contributions between the attractive pEDA terms $\div E_{elstat}$ and $\div E_{orb}$. [d] Percentage values: Relative contributions to the orbital interaction $\div E_{orb}$. [e] Energies computed using a plane wave basis set given in parentheses.

$\Delta\rho_1$(DB intermediate)
$\Delta E_1 = -212$, $\nu_1 = \pm0.76$

THF LUMO at
TS(DB→C)
(−1.89 eV)

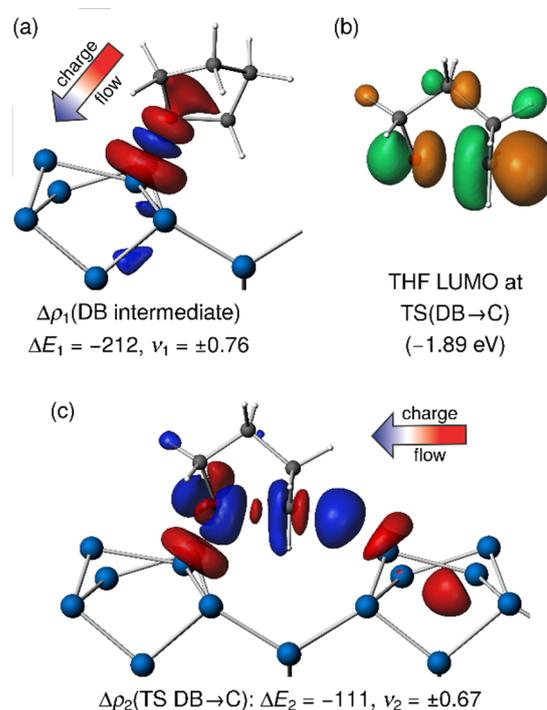$\Delta\rho_2$(TS DB→C): $\Delta E_2 = -111$, $\nu_2 = \pm0.67$

Figure 1. a) Bonding analysis (pEDA) deformation density $\div \psi_1$ at the DB structure of **1** (step 1) showing electron density transfer mainly from a p orbital shaped density at the molecule (red lobes) to the O-Si bonding region (blue lobes). b) LUMO of **1** in the TS(DB→C) geometry. c) pEDA deformation density $\div \psi_2$ at the TS(DB→C) geometry (step 2) showing mainly how a ω^*(C-O) type density (blue lobes) is populated by electrons from the opposing surface dimer row (red lobes). Energies $\div E_i$ in kJ mol^{-1}, eigenvalues τ_i in q_e.

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Adding further minor contributions of the same bonding character, the total stabilization due to dative bond formation can be determined as −293 kJ mol⁻¹, 85% of the orbital term $\div E_{orb}$.[24] Hence, this structure undoubtedly represents a dative bond with ω and φ donation of the non-bonding electron pairs at O toward the surface. This explains the high bonding energy E_{bond} of −134 kJ mol⁻¹, which is the strongest known oxygen dative bond on the Si(001) surface.[25] Considering the loss of entropy upon adsorption,[26] the resulting Gibbs bonding energy (G_{bond}) is −69 kJ mol⁻¹, a value that is in excellent agreement with the experimental value of −60±8 kJ mol⁻¹ determined for **2**.[13c]

To address the regioselectivity in step 2, reaction energies E_{react} and activation energies E_a were calculated for all three possible products (Table 2). While reaction via atom **A** results in the most stable product (E_{react} = −177 kJ mol⁻¹), the corresponding energy barrier (E_a) is actually the highest at 107 kJ mol⁻¹.[27] This is because **A** is located on the same dimer the molecule is bound to and thereby too close for a back side attack at C_ζ. As a consequence, the attack has to occur from the side of the C-O bond, which is reflected in an acute angle ζ^{TS}(O-C-Si) of 65.6° and elongated bonds of d^{TS}(C-O) = 2.289 Å and d^{TS}(C-Si) = 3.374 Å at the TS geometry (Gas phase: d(C-O) = 1.441 Å, DB structure: 1.490 Å) In contrast, reactions via atoms **B** and **C** can occur from the back side. In case of **B** though, E_a is only marginally lower at 100 kJ mol⁻¹, which is again due to a non-ideal TS geometry with an angle of 117.2° and a long C-O bond (2.121 Å). In the attack of **C**, however, ζ^{TS} is much closer to linearity (157.4°), resulting in much shorter bonds at the TS (d^{TS}(C-O/C-Si) = 1.932/2.763 Å) and a drastically lowered E_a value of 53 kJ mol⁻¹ (the G_a value of 50 kJ mol⁻¹ is comparing well to the experimental value of 37±5 kJ mol⁻¹ for **2**[13c]). This confirms the initially made assumption that the main product occurs for the reaction with a TS structure that most closely resembles the bipyramidal TS of S_N2 reactions.

Notably, the anticorrelation of E_{react} and E_a is an exception to the Bell-Evans-Polanyi (BEP) principle, which states that the reaction to the most stable product will have the lowest activation energy[28] and is widely applied in heterogeneous catalysis.[29]

However, this anticorrelation was also found for other molecules adsorbing on Si(001), e.g. primary and secondary alkylamines,[30] so it might be a rather common phenomenon for adsorption on this surface.

Finally, the TS geometry of the attack by atom **C** can be analyzed using pEDA to obtain further insight. The results (Table 1) show that while dispersion contributions barely change compared to the DB structure, electronic effects become significantly stronger and orbital interaction has risen to a value (48% of the attractive terms) where it is almost equally as strong as electrostatics (52%). This is caused by a new orbital contribution with an energy of −111 kJ mol⁻¹ (20% of $\div E_{orb}$, Figure 1c) in addition to the persistent dative bond type interaction (−397 kJ mol⁻¹, 71% of $\div E_{orb}$; Figure S14). Using NOCV analysis, it can be assigned to a nucleophilic attack: The corresponding deformation density (Figure 1c) shows that the molecular LUMO (Figure 1b), an antibonding ω*(C-O) orbital, is populated by electrons from the occupied orbital at the opposing Si_{up} atom **C**.[31] Additionally, the largest electron-accepting region (blue lobe) is located between the attacking silicon and the attacked carbon atom, which highlights that the same electron rearrangement that forms this ω bond also breaks the C-O bond. This perfectly illustrates that the reaction occurs via a single-step nucleophilic substitution mechanism of type S_N2.[32]

In summary, our computational analysis has shown that bonding, reactivity and regioselectivity in this prime model system proceed very similarly to textbook organic chemistry reactions. This demonstrates that even under the conditions of ultra-high vacuum on surfaces, which differ from the usual solvent-based conditions of chemistry, simple chemical concepts are applicable and allow predictability. Our applied computational analysis, however, additionally gives a quantitative insight that goes beyond the pure application of these concepts. The reported nucleophilic substitution reaction can be expected to occur for any molecule with a Lewis basic group and a nearby carbon atom that can be attacked, as previous studies of alcohols,[33] amines,[34] haloalkanes,[17a,17b,17e] organophosphorus[17d] and organosulfur compounds[17c] on Si(001) and Ge(001) have shown. This establishes nucleophilic substitution as a common class of surface reaction on semiconductor surfaces analogous to organic chemistry along with the well-known cycloaddition, dative bond formation, dissociative addition and elimination reactions.[35] The fact that an insertion reaction has been reported as well[36] shows that there are many other bonding and reaction types between molecules and surfaces still waiting to be discovered.

Table 2. Reaction energies E_{react}, activation energies E_a and optimized transition state (TS) distances d^{TS} and angle ζ^{TS} of the C-O bond being broken and the C-Si bond being formed in the S_N2 attack of surface atom **A**, **B** or **C** (see Scheme 3).[a]

Reaction via	E_{react} (G_{react})[b]	E_a (G_a)[b]	d^{TS}(C-O/Si)	ζ^{TS}(O-C-Si)
A	−177 (−176)	107 (94)	2.289/3.374	65.6
B	−163 (−162)	100 (94)	2.121/2.904	117.2
C	−144 (−139)	53 (50)	1.932/2.763	157.4

[a] All energies given relative to the energy of the dative bond structure in kJ mol⁻¹, calculated using PBE-D3(PAW). Gibbs energies G_{react} and G_a calculated at 300 K, 1 bar. Distances d^{TS} given in Å, angles ζ^{TS} in degrees. A detailed conformational analysis was performed (see Supporting Information). [b] Hybrid functional values (HSE06-D3, Supporting Information) showed no qualitative differences.

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Computational Methods

All energies and structures were calculated using density functional theory with periodic boundary conditions as implemented in the Vienna ab initio simulation package (VASP)[38] with the PBE[39] and HSE06[40] functionals (optimizations done using PBE), the DFT-D3 dispersion correction[41] and the PAW formalism[42] (E_{cutoff} = 400 eV). The surface was modeled in frozen double layer approximation (six layers) with at least 10 Å vacuum and cell sizes of 4×2 (4×4 for reaction **B**). Electronic k space was sampled using a grid of B(221) for 4×4 and B(241) for 4×2 cells. Gibbs energies (T = 300 K, p = 1 bar) were calculated in an approach described elsewhere[26] using harmonic frequencies obtained numerically by cartesian displacements of 0.01 Å. TS structures were calculated using the Climbing-image Nudged Elastic Band[43] and Dimer[44] methods. The pEDA bonding analysis was done at PBE-D3/TZ2P, B only k point sampling using closed-shell singlet fragmentation as implemented in ADF-BAND 2016.[45] The approach outlined delivered accurate results for organic/semiconductor systems in the past.[8b,26,46]

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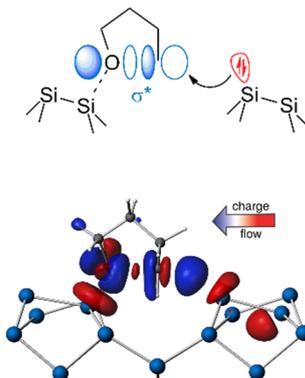
Lisa Pecher, Slimane Laref, Marc Raupach, Ralf Tonner*

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Ethers on Si(001): A prime example for the common ground between surface science and molecular organic chemistry