Lattice Resistance to Hydrolysis of Si−O−Si Bonds of Silicate Minerals: Ab Initio Calculations of a Single Water Attack onto the (001) and (111) β-Cristobalite Surfaces

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Hydrolysis of Si−O−Si linkages of β-cristobalite by a single H_2O molecule is studied within the cluster approach at the DFT (B3LYP) and MP2 levels of theory. The 6-31G(d) and 6-311G(d) basis sets are used. Cluster models, including from 6 up to 14 Si atoms, of the (001) and (111) surface planes are considered. These models are specially designed to take into account the steric constraints imposed by the solid matrix on the Si−O−Si linkages and their nearest surroundings. For comparison, the hydrolysis of the Si−O−Si bridge of the free $(HO)_3Si−O−Si(OH)_3$ molecule is also calculated. The computed activation energy of the reaction (ΔE_a) for the (001) and (111) planes of β-cristobalite is larger by 5 and 16 kcal/mol, respectively, than for $(HO)_3Si−O−Si(OH)_3$ (17 kcal/mol). The higher energy barrier for the surface is due to the resistance of the lattice to the relaxation of the activated complex of the reaction. The difference in ΔE_a between the (001) and (111) planes suggests that the larger the number of Si−O−Si bridges for a Si atom (2 for the (001) plane and 3 for the (111) plane), the stronger the resistance of the solid matrix to the hydrolysis of a Si−O−Si bridge. This finding allows for the atomic-level substantiation of the earlier hypotheses that (i) the hydrolysis of the first Si−O−Si linkage of a Si atom should be the rate-limiting step for the release of Si-$(OH)_4$ and (ii) the dissolution should preferentially take place for the low-linked Si species of the surface. The OH groups produced by the reaction form H-bonds with the nearby Si−OH and Si−O−Si surface species. For both planes, the energy of the reaction (ΔE_r) is within the 1−2 kcal/mol range.

Introduction

The weathering and dissolution of the Earth's crust silicate minerals have raised significant interest due to the global changes in the environmental chemistry caused by human activities.[1,2] It is currently assumed that the hydrolysis of Si−O−Si linkages is the key reaction dominating these geochemical processes.[3−6] Therefore, the fundamental mechanisms affecting the rate of this reaction should be understood for predicting the effects of these environmental changes.

Although under natural conditions, the discussed reaction depends on many chemical factors (solvent effect, pH, saturation index, salt concentration, etc.), even such a simplified model of this reaction as the hydrolysis of a Si−O−Si bond by a single H_2O molecule is very useful for stimulating insight into the atomic-level mechanisms of the aforementioned processes. This reaction has been studied by Xiao and Lasaga[7] for the $(HO)_3$-Si−O−Si(OH)_3$ + H_2O molecular system at the SCF/6-31G(d) and MP2/6-31G(d) levels of theory. These authors have also investigated the hydrolysis pathways for systems $H_3Si−O−SiH_3$ + H_3O^+ and $(HO)_3Si−O−Si(OH)_2O^−$ + H_2O[7,8] in order to elucidate the effects of H^+ and $OH^−$ on this reaction in solution. Based on the obtained differences in geometry between $Si(OH)_4$, $LiOSi(OH)_3$, and $NaOSi(OH)_3$ ab initio molecular models, Gibbs et al.[9−11] have speculated on the effect of alkali cations on the

strength of the Si−O bonds and the accessibility of water to the Si−O−Si bridges of the surface. Using the $(HO)_3Si−O−Si(OH)_3$ molecular model of the siloxane bridge, Strandh et al.[12] have performed DFT (B3LYP) calculations on the effect of protonation and of adsorption of alkali cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) on the Si−O−Si bond strength in silicate minerals.

The geometry of the $O_3Si−O−SiO_3$ group in the activated complex of this reaction[7] differs substantially from the equilibrium geometry of the regular $O_3Si−O−SiO_3$ silica groups.[13,14] Consequently, the elementary act of dissolution of a Si−O−Si linkage may be accompanied by localized structural tensions of the surrounding lattice. These tensions are peculiar to this bond-breaking process and different from a mechanically induced strain on the crystal. Such resistance to the relaxation of the activated complex should increase the activation energy of the reaction. This effect of reaction-induced local strains on the activated complex has been neglected in the previous quantum chemical studies and has never been discussed as a factor of influence on ΔE_a.[7−12]

To examine this effect, we perform ab initio calculations on the hydrolysis of Si−O−Si by a single H_2O molecule for cluster models of the (001) and (111) planes of β-cristobalite. In our study, these β-cristobalite planes represent silicate surfaces with doubly and triply linked Si atoms, respectively. The surface models are specially designed to include the structural restrictions imposed by the lattice on the Si−O−Si group and its nearest surroundings. To evaluate the contribution of this effect to ΔE_a, we compare the computed activation energies of the

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TABLE 1: Activation Energies ΔE_a, and Reaction Energies, ΔE_r, of the Si$-$O$-$Si Hydrolysis (in kcal/mol)

|	$\Delta E_a{}^a$			$\Delta E_r{}^b$
model	DFT/ 6-31G(d)	MP2/ 6-31G(d)	DFT/ 6-311G(d)	DFT/ 6-31G(d)
$H_6O_7Si_2 + H_2O$	17.5	16.9	17.3	5.3
2a	22.8 (22.3)^d			1.1 (-2.5)^f
2b	33.1 (33.8)^d			1.8 (-2.0)^f
2c^c	48.5^d			
2a′^{c}	22.0^d			
2b′^{c}	32.9^d			
2c′^{c}	38.8^{d,e}			

^{a} $\Delta E_a = E(\text{activated complex}) - E(\text{reagents})$. ^{b} $\Delta E_r = E(\text{product}) - E(\text{reagents})$. ^{c} The exact transition-state geometry could not be determined using the available GAUSSIAN-94 options. ^{d} Approximate values (cf. Details of Calculations). ^{e} Affected by the H-bonding interaction with a nearby surface OH group (Figure 6). ^{f} Not BSSE-corrected values.

reaction for the surface with that for the free (HO)$_3$Si$-$O$-$Si-(OH)$_3$ molecule.

Details of Calculations

DFT and MP2 calculations were performed with the GAUS-SIAN-94 package.[13] For DFT calculations, the hybrid B3LYP functional[14] was employed, which is a parametrized combination of the Becke exchange functional,[15] the Lee, Yang, and Parr correlation functional,[16] and the exact Hartree$-$Fock exchange. The standard 6-31G(d) and 6-311G(d) basis sets were used. Corrections for the basis set superposition error (BSSE) were estimated by the counterpoise method.[17] Only a few geometry parameters of the optimized cluster models are reported. The remaining geometry can be obtained from the authors upon request.

The β-cristobalite surface was modeled within the cluster approach.[18] As is commonly accepted for silica and silica-containing oxides,[19] the "dangling" valences of the border Si atoms were saturated with H atoms.
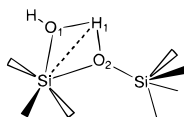
Calculation of the activated complexes was done in two steps. First, the geometry was optimized provided that $\angle O_1SiH_1 = \angle H_1SiO_2$ and $R_{SiO1} = R_{SiO2}$. Then, this optimized geometry was used as the initial geometry for determining the transition state by means of the GAUSSIAN-94 OPT procedure. Our calculations show that this refinement of the geometry insignificantly changes the energy (within 0.7 kcal/mol). Therefore, when the exact transition-state geometry could not be determined with the available GAUSSIAN-94 options (see below), the activation energy obtained in the first step of optimization was used as an approximate ΔE_a value.

When evaluating ΔE_a, we do not include the zero-point vibration energy. The zero-point correction might change the estimated ΔE_a within about ± 1 kcal/mol only,[7,8] which is unimportant for the conclusions made in our study.

Results and Discussion

In Table 1 we present the B3LYP/6-31G(d) activation and reaction energies for the dissolution of the Si$-$O$-$Si bonds of cluster models **1a** and **1b** (Figures 1 and 2). These models mimic the (001) and (111) planes of the β-cristobalite surface,
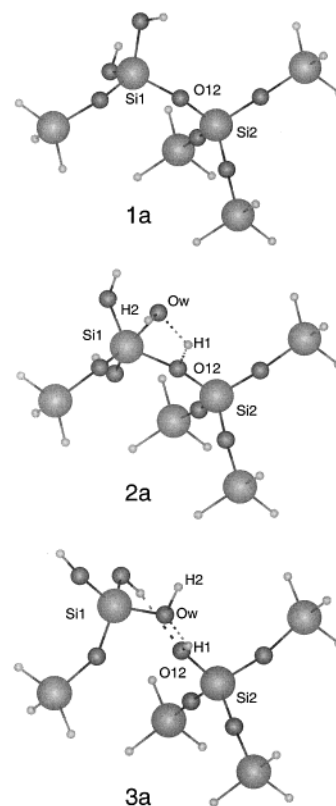

Figure 1. Cluster models of a siloxane bridge (**1a**), the activation complex of its hydrolysis (**2a**), and the hydrolyzed state of this bridge (**3a**) at the (001) β-cristobalite surface. For all models, the position of the border SiH$_3$ groups is identical and fixed, modeling the structural constrains imposed by the lattice.

respectively. For the hydrolysis of the Si(2)$-$O$-$Si(4)/Si(3)$-$O$-$Si(4) bridges of the (001)/(111) plane (2, 3, and 4 designate the number of the Si$-$O$-$Si linkages to the surface), the water attack onto the Si(2)/Si(3) atom of the lowest connectivity to the surface is considered, which should correspond to the lowest activation energy. For both models, the calculations were performed as follows:

1. The cluster model of the bulk (**1**, Figure 3) was optimized with (i) the SiSiSi bond angles and the SiSiSiSi dihedral angles being kept equal to those of the ideal β-cristobalite[20,21] and (ii) the Si$-$H bonds modeling the interaction of the border Si atoms with the lattice being directed similar to the related "broken" Si$-$O bonds. These restrictions make the relaxed bulk cluster correspond in symmetry to the β-cristobalite lattice. This optimization was done to avoid spurious tensions of the surface models that might be caused by the difference between the optimal theoretical and experimental Si$-$O bond lengths.

2. The models of the (001) (**1a**) and (111) (**1b**) planes were produced from model **1** by replacing the relevant SiH$_3$ groups with H atoms. The cluster models of surface (**1a** and **1b**), activated complexes (**2a** and **2b**), and hydrolyzed Si$-$O$-$Si bonds (**3a** and **3b**) (Figures 1 and 2) were fully optimized except for the positions of the border SiH$_3$ groups, which were identical to the positions of the related SiH$_3$ groups of the bulk model **1**. These fixed SiH$_3$ groups mimic the structural restrictions imposed by the cristobalite lattice.

The optimized distances $R_{SiSi}(H_3Si-O-SiO_3) = 3.25$ Å and $R_{SiSi}(O_3Si-O-SiO_3) = 3.24$ Å of model **1** are close to the experimental distance $R_{SiSi} = 3.10$ Å.[21] Similar to the ideal β-cristobalite,[21] all optimized Si$-$O$-$Si bonds of model **1** are nearly linear. As distinct from the bulk and the relaxed (111) surface, the SiOSi bond angle of the relaxed (001) surface nearly

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TABLE 2: Selected Geometry Parameters of Cluster Models (Bond Lengths in Å, Bond Angles in Degrees)

model	Si1−O12	Si2−O12	Si1−Ow	Si2−Ow	O12−H1	O−H1	O−H2	Si1−O12−Si2
1	1.62	1.62						180
1a	1.64	1.63						147
1a′[a]	1.64	1.64						145
1b	1.63	1.62						178
1b′[a]	1.63	1.62						179
1c′[a]	1.62	1.62						177
2a	1.85	1.68	1.88		1.09	1.40	0.97	146
2a′	1.87	1.66	1.87		1.21	1.21	0.97	145
2b	1.97	1.64	1.87		1.12	1.32	0.97	168
2b′	1.92	1.66	1.91		1.21	1.21	0.97	167
2c	1.64	1.92		1.92	1.20	1.20	0.97	172
2c′	1.65	1.86		1.86	1.20	1.20	0.98	173
3a		1.64	1.67		0.98	1.93	0.97	
3b		1.64	1.64		0.98	2.09	0.98	
Si$_2$O$_7$H$_6$	1.65	1.65						124
Si$_2$O$_7$H$_6$·H$_2$O	1.94	1.65	1.83		1.25	1.18	0.97	129

[a] Not presented in the Figures.
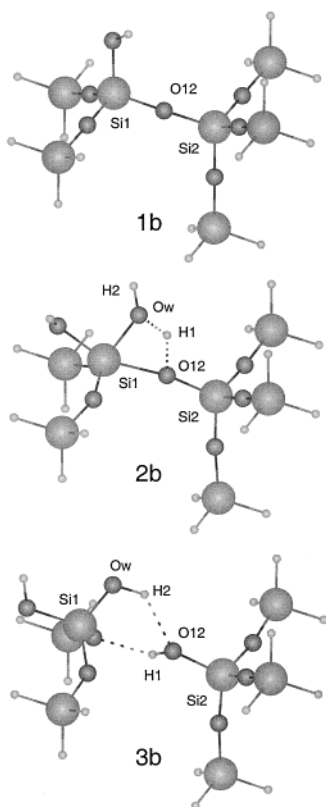
Figure 2. Cluster models of a siloxane bridge (**1b**), the activation complex of its hydrolysis (**2b**), and the hydrolyzed state of this bridge (**3b**) at the (111) β-cristobalite surface. For all models, the position of the border SiH$_3$ groups is identical and fixed, modeling the structural constrains imposed by the lattice.

Figure 3. Cluster model of the β-cristobalite bulk (**1**) used for determination of the position of the border SiH$_3$ groups for models **1a** and **1b**.
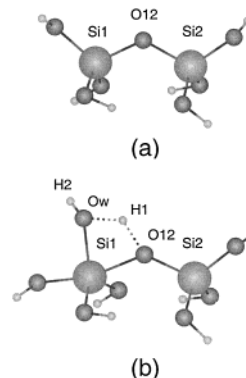
Figure 4. (HO$_3$SiOSi(OH)$_3$ (a) and the activated complex of the hydrolysis of its Si−O−Si bridge (b).

corresponds to the averaged value of 145° for silicates[7] (Figures 1, 2, and 3). Bond lengths and bond angles of the cluster models are given in Table 2.

To compare the Si−O−Si dissolution at the surface with the related gas-phase reaction, we computed the transition state of the Si−O−Si hydrolysis for the free (HO)$_3$Si−O−Si(OH)$_3$ molecule (Figure 4). These calculations were carried out at the B3LYP/6-31G(d), MP2/6-31G(d), and B3LYP/6-311G(d) levels of theory. The difference between the corresponding ΔE_a energies is within 0.6 kcal/mol, suggesting that neither another method of inclusion of electron correlation nor an increase of the basis set should significantly affect the results.

For the (001) and (111) β-cristobalite planes, the activation energy of the hydrolysis is larger than for the molecule

(HO)$_3$Si−O−Si(OH)$_3$ by 5 and 16 kcal/mol, respectively. This result supports our initial hypothesis that the silicate lattice can strongly affect ΔE_a by hindering the relaxation of the activated complex of the reaction. The activation energy increases by 11 kcal/mol on going from the Si(2)−O bond of the (001) plane to the Si(3)−O bond of the (111) plane. This fact suggests that the larger the number of Si−O−Si bonds of a Si atom, the stronger the resistance of the solid matrix to the dissolution of a Si−O−Si bond (see also the activation energy for the hydrolysis of a Si(4)−O bond at the (001) plane below).

In solution, on going from Si(2) to Si(3), apart from the lattice resistance the activation energy may be affected by many other factors. The increase of the number of Si−O−Si linkages decreases the number of terminal OH groups at the Si atom. The related changes in structure and chemical composition of the surrounding solution may influence (i) the accessibility of

water to Si,[9−11,22] (ii) the solvation of the activated complex, (iii) the proton exchange between the site and solution, and (iv) the structural tensions imposed by solution on the site. An unambiguous supposition about the extent to which the reaction rate can be affected by any of these other factors is hardly possible at the present time. Irrespective of this reasoning, the fact that the change in connectivity can change the activation energy by about 10 kcal/mol suggests the discussed effect to be an important factor of influence on the rate of dissolution of silicate minerals. To note, assuming that the contributions of different factors to ΔE_a is about additive, at room temperature the determined difference of ∼10 kcal/mol between the Si(2) and Si(3) species should result in the release of Si(3) being slower by a factor of ∼5 × 10^{-8}.

Models **3a** and **3b** imitate the Si(1)−OH + HO−Si(3) and Si(2)−OH + HO−Si(3) pairs of OH groups produced, respectively, by the hydrolysis of the Si(2)−O-Si(4) and Si(3)−O-Si(4) linkages. These models show that two OH groups formed by these elementary reactions are optimally arranged for the H-bonding interaction with each other (Figures 1 and 2). Moreover, the 2-fold H-bonding interaction takes place for HO−Si(3) in both cases. For Si(1)−OH + HO−Si(3), HO−Si(3) acts simultaneously as a proton acceptor and as a proton donor toward two geminal Si(1)−OH groups. For Si(2)−OH + HO−Si(3), such interaction of HO−Si(3) with both the geminal Si-(2)−OH groups is prohibited owing to the unfavorable position of one of these Si(2)−OH groups (Figure 1). In this case, HO−Si(3) interacts as a proton acceptor with the nearest Si(2)−OH group and as a proton donor with a nearby Si(2)−O−Si(4) linkage. These two H-bonding interactions are analogous to the 2-fold H-bonding interactions of H_2O and CH_3OH with the O_2-$Si(OH)_2$ and O_3SiOH groups of silica.[23]

To check our assumption that the dissolution of a siloxane bridge should preferentially take place at the Si atom of the lowest connectivity to the surface, we calculated the activated complexes of the hydrolysis for a Si(3)−O-Si(4) linkage of the (111) plane at the Si(4) atom (Figure 5, model **2c**). The corresponding activation energy of 48.5 kcal/mol substantially exceeds the activation energy for the dissolution of this bridge at the Si(3) atom (Table 1). This result supports our supposition.

The increase of the size of cluster models should increase the number of degrees of freedom allowed to relax. This may decrease the computed activation energies. To check this suggestion, we calculated ΔE_a for extended analogues of models **2a** and **2b** (**2a′** and **2b′**, Figure 6). The increase of the cluster size insignificantly affects the activation energies (within 0.9 kcal/mol, cf. Table 1). This suggests the ΔE_a values to be quite insensitive to extension of cluster models. The analogous examination of the cluster size effect for model **2c** was impossible because in the related extended model, the activated complex is involved in H-bonding interactions with the surrounding Si−OH groups (Figure 5, model **2c′**). Presumably, this additional interaction is mainly responsible for the difference in activation energy between models **2c** and **2c′** (Table 1).

Conclusion

Summarizing, our calculations suggest that the activation energy of hydrolysis of silicate Si−O−Si bridges should strongly depend on their connectivity to the solid matrix. This effect is due to the steric constraints imposed by the solid on the relaxation of the activated complex of the hydrolysis. The estimated activation energies for the dissolution of Si−O−Si bridges at the double-, triple-, and quadruple-linked Si species
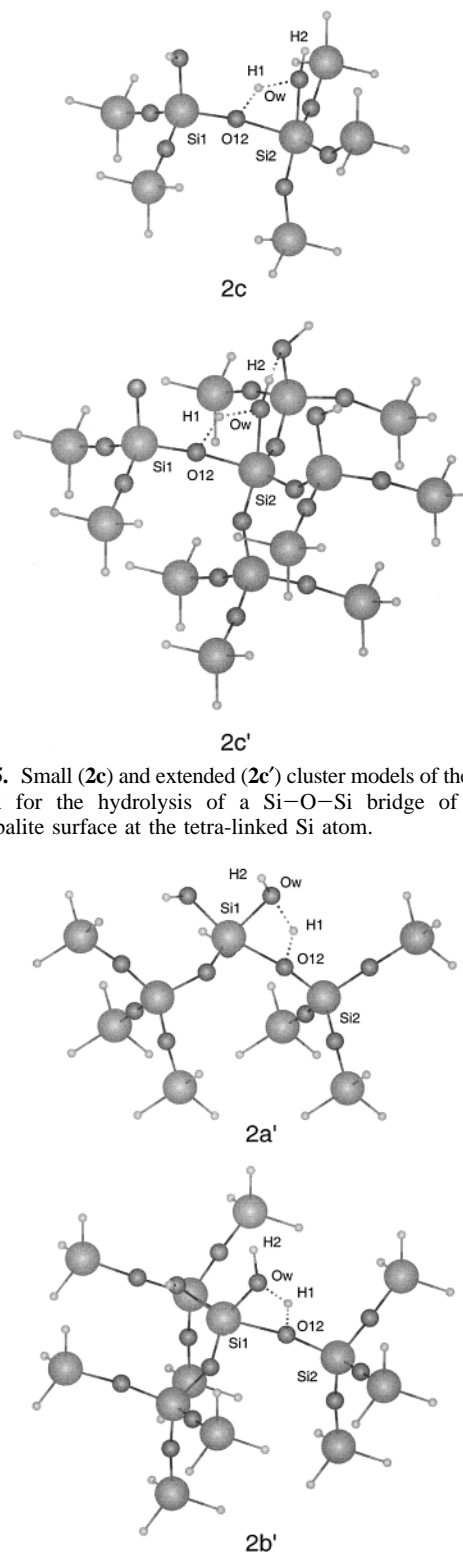

Figure 5. Small (**2c**) and extended (**2c′**) cluster models of the activation complex for the hydrolysis of a Si−O−Si bridge of the (111) β-cristobalite surface at the tetra-linked Si atom.

Figure 6. Extended analogues of the **2a** (**2a′**) and **2b** (**2b′**) models used for checking the cluster size effect on the calculated activation energies.

(22, 33, and 49 kcal/mol, respectively) show that the larger the number of Si−O−Si linkages of a Si species, the higher the energy barrier for the hydrolysis of the Si−O−Si bond. Experimental and theoretical studies have postulated[23,24] that (i) the dissolution of the first Si−O−Si bridge of a Si species is the rate-limiting step for the release of $Si(OH)_4$ and that (ii) the dissolution rate strongly decreases in the series single-linked > double-linked > triple-linked Si species. We propose that

these important features of the dissolution kinetics are mainly accounted for by the described lattice effect.

The rate of dissolution of freshly ground quartz powders in water is experimentally known to gradually decrease with respect to time. For example, a rate of 10^{-15} mol cm^{-2} s^{-1} was determined[25] after a reaction time of 720 h, a rate of 4×10^{-17} mol cm^{-2} s^{-1} was found[26] after 800 h, and a very low reaction rate of 6×10^{-19} mol cm^{-2} s^{-1} was obtained[27] for extremely long (21 000 h) reaction times. This experimental trend conforms to our results. The powdered crystals initially contain a large number of defect Si sites with a low connectivity to the lattice. These sites are the first to dissolve because the activation energy for the rate-limiting breaking of the first Si—O bond is the lowest for them. As the surface fraction of these sites decreases, the reaction rate also decreases, with the final rate being dominated by the dissolution of the high-linked Si species.[28]

It is to be noted that experimental studies have shown little evidence that static strains at surface dislocations increase the rate of mineral dissolution, although the excavation of strained sites at dissolving mineral surfaces is conspicuous.[29] A discussion of the effect of such strains on the activation energy of the reaction requires the relevant quantum chemical calculations. Distinct from the static strains that influence the reaction only at dislocations, the discussed reaction-induced local strains affect all the elementary acts of dissolution.

Our findings furthermore imply that the discussed lattice effect should be included when developing theoretical models for the calculation of activation energies associated with bond-breaking in a crystal environment.

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