Silica dissolution catalyzed by NaOH: Reaction kinetics and energy barriers simulated by quantum mechanical strategies

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Quartz dissolves in Na⁺ solutions much faster than in pure water though the experimental activation energies are essentially the same. To elucidate the mechanism, silica dissolution was simulated using Gaussian 03 software at B3LYP/3-21G* initially and the B3LYP/6-311G(2d,p) levels, applied to a modeled silica Si₄O₆(OH)₄ in the presence of an NaOH molecule and up to five water molecules. Each water molecule was added one by one to the system and approached the surface silicon in successive geometry optimizations. The atomic positions of the sodium hydroxide, the water molecules and the surface SiO₃(OH) moiety were varied to mimic the surface reaction whereas the positions of the remaining SiO₃(OH) atoms were frozen to represent the bulk structure throughout the geometry optimization.

In the first step a single H₂O molecule was added to the system [Si₄O₆(OH)₄ + NaOH]. None of the Si-O bonded interactions were ruptured by the intrusion of the water molecule but the surface Si was stabilized in the Q³Si site (connected to three Si-O-Si bridges), being coordinated by five oxygen atoms. The energy barrier was 63 kJ/mol.

In each of the second and third steps one more water molecule was introduced to the system. One Si-O bonded interaction of the Si-O-Si bridges was ruptured to make Q²Si and Q¹Si sites in the second and third steps, respectively, and the energy barriers were low (22–29 kJ/mol).

In the fourth and fifth steps, the added water molecules were prevented by the sodium ion from reaching the last Si-O-Si bridge, leaving the Si in the Q¹Si site.

The basis set was raised to the 6-311G(2d,p) level and applied to the 63 kJ/mol barrier found in the first step to determine the maximum energy barrier in the series of reactions. The barrier increased to 88 kJ/mol (82 kJ/mol in enthalpy), which is still in the range of experimental activation energies of 46–96 kJ/mol.

In summary sodium works to stabilize the surface silicon in penta-coordination with the energy barrier, 82 kJ/mol, resulting in longer Si-O distances and the weakening of the bonded interactions. This makes the Si-O rupture easier and faster, which gives insight as to how the presence of alkali enhances silica dissolution.

Keywords: Sodium hydroxide, Gaussian 03, Activation energy, Geometry optimization, Alkali enhancement

INTRODUCTION

Understanding the interaction of water with the Si-O bonded interaction is key to interpreting many important geological and geochemical processes. For example, rock strength is affected by hydrolytic weakening (e.g., Tullis and Yund, 1980, 1989). The full range of water–rock interactions found in magma generation and evolution (Burnham 1997), metamorphism (Spear, 1993), wall rock alteration (Reed, 1997) and chemical weathering (White and Brantley, 1995) involve the reaction of water with Si–O bonded interactions. In the waters in the natural en-
environment, alkali ions are commonly present and play an important role in water-rock interactions. It is, therefore, of great value to investigate the interaction of Si-O bonds and water in the presence of alkali ions.

Numerous experimental studies of the kinetics of silica dissolution reactions, reviewed by Dove and Rimstidt (1994), provide base-line information about the nature of the silica-water interaction. In these studies the activation energies for quartz dissolution were estimated to be roughly 75 kJ/mol (18 kcal/mol) although there is a large scatter (46-96 kJ/mol) around this value (Table 1). It is well known that silica dissolution is endothermic reaction (Iler, 1979) and that the presence of alkali cations like Na and K enhances the dissolution rate. For example, Dove and Crerar (1990) determined the quartz dissolution rates at near-neutral pH in the solutions with as little as 0.05 molal NaCl or KCl concentrations at the hydrothermal conditions of 100 °C to 300 °C, and found that the rate is enhanced by a factor of 33. In spite of the alkali enhancement, the activation energies in the presence of alkali cations (71.2 kJ/mol for NaCl and 71.5 kJ/mol for KCl) are reported by them to be the same as that in the deionized solution (71.3 kJ/mol). Thus, the activation energies so far reported are in the same range as for silica dissolution in deionized water. The reason for the alkali enhancement is still unclear.

On the other hand, theoretical tools of computational chemistry, such as molecular dynamics and molecular orbital geometry optimization strategies, enabled the modeling of surface reactions at the atomic level (Lasaga, 1995;Felipe et al., 2001). In an earlier study, Lasaga and Gibbs (1990) pointed out that the reaction, \( \text{H}_2\text{O} + \equiv\text{Si-O-Si}^- \rightarrow 2 \equiv\text{Si-O-H} \), is an elementary step in the hydrolysis process occurring at the surface of silicate. Subsequent studies have been carried out in an attempt to clarify the silica dissolution kinetics (Xiao and Lasaga, 1994, 1996; Walsh et al., 2000; Criscenti et al., 2006; Nangia and Garrison, 2008, 2009).

Several studies have simulated the hydrolysis of silica surfaces using molecular dynamics strategies (Cheng et al., 2002; Du et al., 2003; Rignanese et al., 2004; Ma et al., 2005). These studies indicate that the attack of water at the defect sites on a silica surface lowers the energy barrier and that the reactions are catalyzed by a cooperative transfer of hydrogen atoms contributed by the water molecules.

<table>
<thead>
<tr>
<th>Table 1. Experimental and calculated activation energies ((E_a), kJ/mol) for silica dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy ((E_a), kJ/mol)</td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td><strong>Experimental</strong></td>
</tr>
<tr>
<td>67.4-76.6</td>
</tr>
<tr>
<td>68.7 (α-cristobalite)</td>
</tr>
<tr>
<td>71.3</td>
</tr>
<tr>
<td>89</td>
</tr>
<tr>
<td>46.0-96.2</td>
</tr>
<tr>
<td>94.9</td>
</tr>
<tr>
<td>72</td>
</tr>
<tr>
<td>83.2</td>
</tr>
<tr>
<td>72.8</td>
</tr>
<tr>
<td>72</td>
</tr>
<tr>
<td><strong>Computational</strong></td>
</tr>
<tr>
<td>119.3 (Q(^4)-&gt;Q(^3))</td>
</tr>
<tr>
<td>122.6 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>116.8 (Q(^2)-&gt;Q(^1))</td>
</tr>
<tr>
<td>75 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>92 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>138 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>205 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>142 (138) (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>115-125 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>152-157 (Q(^3)-&gt;Q(^2))</td>
</tr>
<tr>
<td>138.9 (Q(^3)-&gt;Q(^2)) Mg(^{2+})</td>
</tr>
<tr>
<td>156.4 (Q(^3)-&gt;Q(^2)) Ca(^{2+})</td>
</tr>
<tr>
<td>82 (Q(^3)-&gt;Q(^2)) Na(^+)</td>
</tr>
</tbody>
</table>

Note: (\(Q^n \rightarrow Q^m\)) indicates the rupture of Si-O-Si bridges connected to Si atom from n bridges to m bridges.
protonated, neutral and deprotonated species (Nangia and Garrison, 2008, 2009).

The Na enhancement of the experimental silica dissolution rate is markedly observed in solutions from neutral to high pH (Dove, 1995). The enhanced rate curve extends smoothly from high to very high pH, which suggests that Na enhances dissolution even in solutions with very high pH. Consequently, we use the sodium hydroxide molecule for modeling the system of silica in basic solution and for simplifying the system.

Sverjensky (2005) used a theoretical framework to predict surface charges on oxides in 1:1 (M⁺;L⁻) electrolyte salt solutions and found that on high dielectric constant solids, such as rutile, the alkali cations predominantly adsorb close to the surface as inner-sphere complexes but on most other oxides, including silica, they predominantly adsorb further away as outer-sphere complexes. This means that most adsorbed sodium ions on a silica surface are present as outer-sphere complexes. However, Sverjensky’s model implies that even though the concentration of adsorbed alkali cations present as inner-sphere complexes is small there is an equilibrium between inner- and outer-sphere cations so that some inner-sphere complexes are present on silica surfaces. Wallace et al. (2010) investigated the effect of both inner- and outer-sphere complexes of Mg²⁺ and Ca²⁺ on the hydrolysis of Si-O bonded interactions and found that the height of the hydrolysis barrier is significantly lower for the inner-sphere site. They concluded that, despite their documented abundance at the silica-water interface, outer-sphere surface complexes are not likely participants in the Si-O bonded dissociation mechanism. Taking these points into account, we designed a simulation model, which considers the effect of sodium ions adsorbed on silica surfaces as inner-sphere complexes because they appear to be the species most likely responsible for the observed increase in dissolution rates.

In this study, we examine the attack of multiple water molecules on a neutral silica surface in the presence of a NaOH molecule. In this dissolution simulation, the strategy is to have each water molecule approach the silica model Si₃O₆(OH)₄, step by step producing the optimized geometry at each step, thereby moving along the energy valley.

The objective of this simulation is to find what are likely to be the intermediate structures and the values of the intermediate energies in a series of reactions. In this way, we are able to obtain insight into the dissolution process that is not possible to observe in experiments, and, therefore, to promote our understanding of silica dissolution catalyzed by sodium hydroxide.

Besides our primary goal of clarifying the dissolution kinetics in the presence of sodium hydroxide, the second goal is to address how the calculated activation energies relate to the experimental ones for silica dissolution with sodium hydroxide.

**COMPUTATION AND RESULTS**

Gaussian 03 (Frisch et al., 2003) and Xtaldraw (Bartelmehs et al., 1993) were used for the ab initio calculations and crystal structure drawings, respectively.

At the silica–water interface, the silica surface is hydroxylated with the major part of the surface consisting of silanol in which the surface silicon is in the Q°Si site (connected to three Si–O–Si bridges and a silanol) (Iler, 1979; Parks, 1984). On this basis, the silica was modeled as a hydrogen clad, Si₃O₆(OH)₄ molecule which was geometry optimized at the B3LYP/6-311G(2d,p) level, assuming S₄ point symmetry. The resulting configuration is composed of four silicate tetrahedra corner sharing each others. This molecule is used to model the silica surface and the matrix by considering it in two parts, one variable surface SiO₂(OH) moiety that is flexible so that it can respond to the water attack and three frozen inner tetrahedra Si₃O₆(OH)₄ matrix used to model the bulk structure.

**First step**

The oxygen atoms of a water molecule and a sodium hydroxide were initially placed 4.3 Å and 3.5 Å respectively from the target surface silicon Si atom as shown in Figure 1. The atomic positions of each of the atoms in the SiO₄(OH) moiety, the sodium hydroxide and the water molecule were free to move during the geometry optimization with the constraint that the Si–O–O distance r (Ow: the water’s oxygen) was fixed at 4.3 Å. As indicated above, the remaining SiO₄(OH)₂ atoms associated with the interior of the silica model were frozen at their initial-ly optimized positions. The geometry optimization of the system was completed at the B3LYP/3-21G* level. After the optimization, the Si–O₆ distance r was decreased by the value Δr, and as before, the positions of the atoms in the SiO₄(OH) moiety, sodium hydroxide and the water molecule were again relaxed during the energy optimization. This strategy was continued with a progressive shortening of the Si–O₆ distance from 4.3 to 1.55 Å. A graph of the total energies was obtained along the potential surface valley of the Si–O₆ pathway as displayed by the curve in Figure 2.

The total energy increased from a distance of 3.4 to 2.3 Å with the slope of the energy curve progressively increasing with decreasing distance. From this energy curve and the geometries, estimates of the adsorption state and...
the transition state were found. The actual modeled adsorption and transition states were found by taking the geometries of the estimated states and optimizing these relaxing the \( \text{Si}_i-\text{O}_w \) distance. The resulting values are plotted in Figure 2. The energy difference between these states was 63 kJ/mol. As the \( \text{Si}_i-\text{O}_w \) distance further decreased, the total energy decreased until a distance of 1.8 Å was obtained. The product geometry was also optimized relaxing \( \text{Si}_i-\text{O}_w \) distance as shown in Figure 3 together with the geometries of adsorption and transition states. Note that the five-fold coordinated silicon atom is sitting at the stable \( Q^3 \text{Si} \) site in the minimum energy configuration. The sodium atom is connected to one of the three bridging oxygen atoms, an oxygen originated from the NaOH molecule and the water’s oxygen. As a result, the sodium atom weakens the Si–O bonded interactions around the surface Si and the Si–O distances are elongated from ~1.65 Å to ~1.75 Å, which are suitable bond lengths for a five-fold coordinated silicon. In previous works, there has been no report that the sodium stabilizes the silicon in the five-fold coordination in the neutral surface condition.

In order to highlight the role of sodium hydroxide in silica dissolution the same calculations were performed setting the model without sodium hydroxide (the model is the same as above but the NaOH molecule is replaced by a water molecule HOH, in which each hydrogen is placed about 1 Å from the water oxygen). A graph of the total energies and the geometries of adsorption and transition states, and product are shown in Figures 4 and 5, respectively. In this case the activation energy from the adsorption state to the transition one is fairly high (112 kJ/mol) and one of three \( \text{Si}-\text{O}–\text{Si} \) bonded interactions is ruptured to make \( Q^2 \text{Si} \) site as shown in the product. This illustrates a clear difference from the process with sodium hydroxide where the Si atom is stabilized in a five-fold coordination and in \( Q^3 \text{Si} \) site. The silicon atom is never stabilized in higher coordinations than four without sodium hydroxide and this is apparently the role that sodium plays in silica-water interactions.

Second step

A second water molecule was added to the product geometry obtained in the first step and the same strategy as in the first step was applied. That is, the atomic positions of surface \( \text{Si}_i \) \( \text{O}_i \text{(OH)} \) moiety, sodium hydroxide and two water molecules were free to move during the geometry optimization. The distance between the target Si and the oxygen \( \text{O}_w \) of the added water molecule were fixed and the geometry was optimized. In this way the optimizations were performed step by step with each step decreasing the \( \text{Si}_i-\text{O}_w \) distance along the energy valley of \( \text{Si}_i-\text{O}_w \) pathway. The energy curve is shown in Figure 6. The energy generally decreases with decreasing distance from 4.0 Å to 2.0 Å (although there is a hump around 3 Å), goes up to a sharp peak at 1.8 Å and falls down to a minimum at 1.7 Å. From the geometries of these constrained optimizations the adsorption state, reactant, transition state and product
were successfully obtained at the distances of 3.5, 2.0, 1.8 and 1.7 Å, respectively. The energy difference between the reactant at 2.0 Å and the transition state at 1.8 Å is 22 kJ/mol, a value far lower than the experimental activation energies. It is reasonable that this low activation energy results from the weakening of the Si-O bonded interaction associated with the five-fold coordination of silicon.

The geometries of these states are shown in Figure 7. The added water molecule approaches the target silicon and

**Figure 3**. The geometries of the adsorption state (r = 3.4 Å), transition state (r = 2.3 Å) and product (r = 1.8 Å) in the first step. The product is characterized by the five-fold coordinated silicon atom.

**Figure 4**. A graph of the total energies for the system SiO₄(OH)₂ + 2H₂O without sodium hydroxide, calculated at the B3LYP/3-21G* level versus the distance r of the water oxygen Oₛ to the target silicon atom Siₜ. At each point the geometry was optimized under the constraint of a fixed r distance. The adsorption state, transition state and product were optimized with the distance constraint removed, starting from the geometries optimized under the constraint.

**Figure 5**. The geometries of the adsorption state (r = 3.6 Å), transition state (r = 1.9 Å) and product (r = 1.7 Å) in the reactions where the NaOH molecule was replaced by a water molecule H₂O. The product is characterized by the rupture of one of three Si-O_bonded interactions to make a Q²Si site keeping the four-fold coordination of Si.

**Figure 6**. A graph of the total energies calculated at the B3LYP/3-21G* level versus the distance r of the water oxygen Oₛ to the target silicon atom Siₜ in the second step. At each point the geometry was optimized under the constraint of a fixed r distance. The adsorption state (r = 3.5 Å), reactant (r = 2.0 Å), transition state (r = 1.8 Å) and product (r = 1.7 Å) were optimized without the distance constraint, starting from the geometries optimized under the constraint.
makes a bonded interaction with the silicon momentarily to form a six-fold coordinated silicon intermediate. It attacks one of the three bridging oxygen atoms, transferring a hydrogen to it in the transition state. As a result, the bridging oxygen moves from the Si atom, which constitutes the rupture of Si-O<sub>w</sub> bonded interaction, leading to the formation of Q<sup>2</sup>Si site. At the end of this step, the sodium atom has caused a weakening of the Si-O bonded interactions, connected to the three oxygen atoms around the target silicon resulting in the five-fold coordinated silicon atom as shown in the product geometry.

**Third step**

A third water molecule was added to the product geometry obtained in the second step and the same strategy as in the previous steps was performed. The energy curve is shown in Figure 8. As the Si-O<sub>w</sub> distance goes from 4.7 Å to 3.5 Å, the energy decreases. The energy increases as the distance decreases from 3.5 Å to around 2.7 Å. Then, it decreases to a minimum at 2.0 Å, again increases to a sharp peak at 1.74 Å and then drops down to a minimum at 1.73 Å. From the geometries of these constrained optimizations the adsorption state, the first maximum (computationally a transition state), the reactant, the transition state and the product were successfully obtained at the distances 3.5, 2.7, 2.0, 1.74 and 1.72 Å, respectively. The energy difference between the adsorption state at 3.5 Å and the first maximum at 2.7 Å is 29 kJ/mol and that between the reactant at 2.0 Å and the transition state at 1.74 Å is 22 kJ/mol. Both of them are far below the experimental activation energies. It is clear that these low activation energies result from the weakening of Si-O bonded interaction associated with the five-fold coordination of silicon. The geometries of these states are shown in Figure 9. After the added water molecule has passed through the distance of the first maximum as it approaches the target silicon, it attacks one of the two Si-O-Si bridging oxygen atoms yielding a hydrogen to that oxygen just before the transition state as shown in the figure at r = 1.8 Å, at which time the target silicon is instantaneously coordinated with six oxygen atoms. As a result the bridging oxygen moves from the Si atom rupturing the Si-O bonded interaction, which leads to the formation of a Q<sup>2</sup>Si site. After this has occurred, the target silicon atom is only connected with the inner matrix by the last Si-O-Si bridging oxygen and is still coordinated by five oxygen atoms as shown in the product geometry.

**Fourth and fifth steps**

In each of the fourth and fifth steps one additional water molecule was added. But these additional water molecules were prevented by the sodium atom from reaching the last Si-O-Si bridge. It is possible that, after the sodium atom is saturated with water molecules, the next one might suc-
cessfully attack the last bridging oxygen to cleave the bridge or the sodium atom might dissolve out into the solution. At this time, the computation needed to explore this is too large.

**Promotion of basis set and correction of energies**

The energy barriers are as low as 22–29 kJ/mol in the second and third steps. The highest barrier occurs in the first step. The basis set was raised from the 3–21G* to the 6–311G(2d,p) level and applied to the transition and adsorption states to better determine the energy barrier. The barrier appreciably increased from the 63 kJ/mol calculated with the less robust basis to 88 kJ/mol as shown in Figure 10. This increase is consistent with the increase that was reported by Nangia and Garrison (2008), associated with the promotion of the basis set from 6–31+G(d,p) to MG3S. Here we performed the vibrational frequency calculation at room temperature. It is difficult to correctly estimate the zero-point vibrational energy since positions of the matrix atoms were fixed in the optimization, but the rough estimation is reasonable because the zero-point vibrational energy itself is small compared with the total energy. It is also true that the matrix atoms are frozen throughout the optimizations for the adsorption state and the transition one, so that the effect on vibrational energies should be nearly equal. The energy difference for this part might, therefore, be cancelled out. The correction value used for the activation energy is 3 kJ/mol, so that the barrier is lowered to 85 kJ/mol. Not only zero point energies ($E_{ZPE}$) of adsorption state and transition state, thermal energies ($E_{\text{therm}}$), thermal enthalpies ($H_{\text{therm}}$), entropies ($S$) and thermal free energies ($G_{\text{therm}}$) are also estimated from the vibrational frequency calculation as listed in Table 2. Activation energy in enthalpy ($\Delta H$) reduced to 82 kJ/mol and that in free energy ($\Delta G$) increased to 91 kJ/mol. The experimental activation energy is best interpreted as the enthalpy of activation ($\Delta H$), i.e. the difference between the enthalpy of formation of the activated com-
get silicon concluded with a five process of moving a water molecule steadily toward a tar-
lake like a ruptured Si-
In the first step in which a water molecule and a sodium Penta-coordination of Si and reaction barriers
negligible. Their difference is 3 kJ/mol, which is mostly 9 and 12 kJ/mol for the reactions with and without NaOH, respectively. The entropy term $T \Delta S$ at the room temperature is 151 kJ/mol, which all demonstrates high bar-
riers when the sodium hydroxide is not introduced in the system. The activation energies $E_a$ for the silica dissolution with
an increase of coordination number, which induces the weakening of Si–O bonded interactions. This weakening suggests that the Si–O connections are susceptible to rupture. It is also important to note that the product is at the stable state having the minimum energy configuration as shown in Figure 2.

In each of the second and third steps a water molecule approached the five-fold coordinated silicon atom and cleaved one of the weakened Si–O$_w$ bonded interactions in each step, with low energy barriers of 22–29 kJ/mol (due to the increase in coordination number). In this process, the $Q^3$Si site changed to a $Q^3$Si and then to a $Q^3$Si site.

Going back to the first goal of this study, the most important factor of the dissolution kinetics in the presence of sodium hydroxide is that sodium plays the role of forming a five-fold coordinated silicon atom, finally keeping the system at the energy minimum. This makes the rupture of the Si–O bonded interactions easier and faster. This result suggests that alkali ions like Li and K and alkali earth ions like Mg and Ca behave in the same way as sodium. Thus, the weakening of the Si–O bonded interactions resulting from the five-fold coordination should be a clue as to the reason for the alkali or alkaline earth enhancement of the silica dissolution.

It is well known that the silicon atom is four-fold co-
ordinated by oxygen atoms in ambient condition. But co-
ordination numbers higher than four have been actually reported in glasses containing alkali oxide in the system of Na$_2$O–SiO$_2$–P$_2$O$_5$ (Dupree et al., 1988, 1989) where the proportion of six-coordinated silicon depends on the alkali content and cooling rate. However, six-coordinated silicon atoms were not observed by NMR spectroscopy in SiO$_2$–P$_2$O$_5$ glasses without Na$_2$O (Weeding et al., 1985). After these reports a number of examples of six-coordinated silicon atoms in SiO$_2$–P$_2$O$_5$ glasses containing alkali oxide have been reported. Recently Ide et al. (2007) studied R$_2$O–SiO$_2$–P$_2$O$_5$ ($R = \text{Li, Na, K}$) glasses and observed six-coordinated silicon atoms in the XANES and XAFS analyses and the fraction of six-coordinated silicon atoms increased with increasing concentration of alkali oxide. Thus, these experimental results support our computa-
tional result that alkali ions help to make silicon atoms be coordinated by more than four oxygen atoms.

Wallace et al. (2010) investigated the ability of M(II) aqua ions to promote the hydrolysis of Si–O bonded inter-
actions using the silica cluster model H$_4$Si$_6$O$_{16}$ and ad-

### Table 2. Activation energies $E_a$ for the silica dissolution with NaOH and without NaOH

<table>
<thead>
<tr>
<th>Energies with NaOH</th>
<th>$E_{diss}$/kJ mol$^{-1}$</th>
<th>$E_{ZPE}$/kJ mol$^{-1}$</th>
<th>$E_{therm}$/kJ mol$^{-1}$</th>
<th>$H_{therm}$/kJ mol$^{-1}$</th>
<th>$S/kJ mol^{-1}$</th>
<th>$G_{therm}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{diss}$/kJ mol$^{-1}$</td>
<td>$E_{ZPE}$/kJ mol$^{-1}$</td>
<td>$E_{therm}$/kJ mol$^{-1}$</td>
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<tr>
<td></td>
<td>0</td>
<td>88</td>
<td>88</td>
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<tr>
<td></td>
<td>346</td>
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<td>249</td>
<td>3</td>
<td>91</td>
<td>0.609</td>
<td>248</td>
</tr>
</tbody>
</table>

Note: The systems in the first step, re-optimized at the B3LYP/6-311G(2d,p) level. Zero point energies ($E_{ZPE}$), thermal energies ($E_{therm}$), thermal enthalpies ($H_{therm}$), entropies ($S$) and thermal free energies ($G_{therm}$) are derived from the vibrational frequency calculation at room temperature (25 °C).

**Discussion**

#### Penta-coordination of Si and reaction barriers

In the first step in which a water molecule and a sodium hydroxide were introduced to the system, nothing drastic like a ruptured Si–O bonded interaction occurred but the process of moving a water molecule steadily toward a target silicon concluded with a five-fold coordinated silicon atom. This is the consequence of the presence of a sodium hydroxide. The connectedness of the $Q^3$Si site doesn’t change but the coordination number of the silicon atom increases from four to five. The energy barrier of this reaction is 63 kJ/mol in the B3LYP/3-21G* level. The distances between Si and coordinated oxygen atoms are lengthened from about 1.65 Å to 1.75 Å associated with the increase of coordination number, which induces the weakening of Si–O bonded interactions. This weakening suggests that the Si–O connections are susceptible to rupture. It is also important to note that the product is at the stable state having the minimum energy configuration as shown in Figure 2.

The same calculations were also applied to the process without NaOH in the first step and the results are listed in Table 2. The barrier appreciably increased from the 112 kJ/mol calculated with the less robust basis to 150 kJ/mol in the same way as above. The activation energies in enthalpy $\Delta H$ and in Gibbs free energy $\Delta G$ are 139 and 151 kJ/mol, respectively, which all demonstrates high bar-
riers when the sodium hydroxide is not introduced in the system. The entropy term $T \Delta S$ at the room temperature is 9 and 12 kJ/mol for the reactions with and without NaOH, respectively. Their difference is 3 kJ/mol, which is mostly negligible.

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sorption complexes of Mg\(^{2+}\)(6H\(_2\)O) and Ca\(^{2+}\)(6H\(_2\)O). The activation free energies are 178.9 (Mg) and 178.8 (Ca) kJ/mol in the outer-sphere adsorption hydrolysis and 138.9 (Mg) and 156.4 (Ca) kJ/mol in the inner-sphere adsorption hydrolysis, which is clearly different from the experimental activation energies and our energy barrier of 82 (Na) kJ/mol.

The second goal for the activation energy is fairly well addressed in this study. The largest energy barrier is not the energy to rupture the Si–O bonded interactions but the energy to form the five-fold coordinated silicon atom in the presence of sodium hydroxide. The barrier is 63 kJ/mol in the 3-21G* level and 88 kJ/mol in the 6-311G(2d,p) level. The value 88 kJ/mol (82 kJ/mol in enthalpy) is fairly high compared with experimental values but is still in the range of experimental ones of 46-96 kJ/mol. The energy barrier of the Si–O rupture for \(Q^1\)Si to \(Q^2\)Si was 22 kJ/mol and that for \(Q^2\)Si to \(Q^4\)Si was 22 or 29 kJ/mol in this study, which does not indicate the special resistance of the bulk structure as Pelmenschikov et al. (2000) reported. This can be explained by the result that the Si–O bonded interactions are already weakened by the five-fold coordination of the silicon atom in the presence of sodium hydroxide, so that the effects of bulk resistance are not explicitly observed in this study.

Cypryk and Aleloig (2002) calculated the activation energies for hydrolysis of siloxanes and siloxanols using water clusters (H\(_2\)O)\(_n\), n = 1, 2, 3, 4 at B3LYP/6-311+G(2d,p) level and found that the energies are reduced from 140 kJ/mol to 74 kJ/mol as the number of water molecules increases, assisted by the cooperative proton transfer from the nucleophile to siloxane oxygen. This is the result in cleaving an Si–O–Si bridge of connectedness (\(Q^2\) → \(Q^4\)) attacked by multiple water molecules. Although the situation is quite different from our case, their result leaves the possibility of a reduction of the activation energy by the attack of multiple water molecules (n>3) on one Si–O–Si bridge, so that the present value 88 kJ/mol (82 kJ/mol in enthalpy) should be the upper limit of the activation energy.

**Dissolution associated with Pelmenschikov’s self-healing effect**

After the third step the target silicon is still five-fold coordinated and left as a \(Q^1\)Si. The fourth and fifth steps were tried adding a water molecule in each case, but the trial failed because the last Si–O–Si bridge formed a narrow bottle neck connecting the surface group and the inner bulk structure, and the sodium prevented the water molecule from entering the bottle neck. In this situation two scenarios seem plausible for the \(Q^3\)Si rupture. The first one is that the last Si–O–Si bridge is ruptured with the low activation energy of 20-30 kJ/mol after the addition of several more water molecules, since the target Si is still coordinated by five oxygen atoms. The second scenario is that the sodium ion dissolves out into the solution by the addition of water molecules and the energy for the hydrolysis of last Si–O–Si bridge is the same as the energy in the deionized water without alkali ions, which conforms with the experimental result. This second scenario also conforms with Pelmenschikov’s proposal. Pelmenschikov et al. (2001) proposed the new mechanism based on the self-healing effect of reactions which makes the preexponential factor extremely small and emphasized the importance that the measured activation energy is associated with the hydrolysis of the last Si–O–Si bond of the Si atoms.

According to the second scenario our results are essentially consistent with Pelmenschikov et al.’s “self-healing” model of silica dissolution and provide a plausible explanation for why silica dissolution in the presence of alkali and alkaline earth ions is 20 to 30 times faster than in pure water even though the observed activation energy is essentially the same for both cases. Dove and Crerar (1990) showed that the dissolution rate of quartz in 0.05 m NaCl solutions is about 30 times faster than in pure water even but activation energies for both cases are essentially the same [\(E_a\)(NaCl) = 71.5 kJ/mol and \(E_a\)(pure water) = 71.3 kJ/mol]. Similarly, Icenhower and Dove (2000) reported that the dissolution rate of amorphous silica in 0.05 m NaCl solutions is about 20 times faster than it is in pure water but the activation energies are nearly the same [\(E_a\)(NaCl) = 74.5 kJ/mol and \(E_a\)(pure water) = 76.4 kJ/mol]. Thus, it seems that Na produces a catalytic effect even though it does not change the experimental activation energy. A reasonable explanation for this effect is that Na does not catalyze the \(Q^1\) → \(Q^3\) detachment reaction, which is the observable step for silica dissolution, but rather it catalyzes prior bond breaking steps in the overall dissolution process such that it increases the concentration of \(Q^3\)Si sites on the silica surface.

The release of dissolved Si from a silica surface involves a chain reaction consisting of three bond breaking steps:

\[Q_1 + H_2O \rightleftharpoons Q_2 + H_2O \rightleftharpoons Q_3 + H_2O \rightleftharpoons H_2SiO_4(aq)\]

(1)

where the overall rate of dissolution is

\[r = k_{-1}a_{H_2O}C_{Q1} - k_{-2}a_{H_2SiO_4}\]

(2)

If the solution is very dilute so \(a_{H_2SiO_4} \approx 0\) and \(a_{H_2O} = 1\), the
observed rate is simply a product of the forward rate constant and the concentration of the $Q^i$Si sites

$$r = k_{+1}C_{Q^i_1}$$  \hspace{1cm} (3)

at steady state

$$k_{-2}C_{Q^i_2} - k_{+2}C_{Q^i_1} = k_{+1}C_{Q^i_1} - k_{-1}m_{H_2SO_4}$$  \hspace{1cm} (4)

the concentration of $Q^i$Si sites depends on the concentration of $Q^2$Si sites

$$C_{Q^i_1} = C_{Q^i_1} \left( \frac{k_{-2}}{k_{+1} + k_{-2}} \right)$$  \hspace{1cm} (5)

The concentration of $Q^i$Si sites depends on the concentration of $Q^2$Si sites in a similar fashion. This chain of reversible elementary reaction steps produce the "self-healing" effect described by Pelmenschikov et al. (2001), which means that the concentration of $Q^2$Si and $Q^3$Si sites is controlled by a sequence of near equilibrium reaction steps. This leads to the conclusion that the measured activation energy for silica dissolution simply reflects the $Q^i$Si to $H_2SiO_4$ reaction and that the overall dissolution rate is low because the concentration of $Q^2$Si sites is low.

The model presented here shows that inner-sphere sorption of Na causes a significant reduction of the activation energy barriers for the $Q^i$Si to $Q^2$Si and $Q^2$Si to $Q^3$Si reactions. This in turn causes the rates of these reactions to increase and increases the concentration of $Q^3$Si sites, which causes an increase in the overall reaction rate. However, our model shows that the $Q^3$Si to $H_2SiO_4$ reaction does not occur as long as the Na remains on the surface but we postulate that Na will eventually become hydrated and depart the surface leaving behind a $Q^i$Si site as indicated above in the second scenario, which then reacts with a water molecule to produce $H_2SiO_4$. Because the more abundant $Q^i$Si sites produced by this Na-catalyzed process are indistinguishable from $Q^2$Si sites produced by the water hydrolysis elementary steps in the absence of Na, the observed rate is increased even though the observed experimental activation energy for the Na-catalyzed reaction is the same as for the reaction in pure water.

This is the dissolution kinetics according to the Pelmenschikov’s self-healing effect (Pelmenschikov et al., 2000, 2001) and all of these discussions emphasizes the importance for determining the kinetics and the energy of hydrolysis for the last Si-O-Si bridge.

CONCLUSIONS

It is found that the presence of sodium atoms plays a role for the formation of five-fold coordinated silicon atoms in the dissolution kinetics of silica, which induces the elongation of the Si-O distances and the weakening of the bonded interactions, making the Si-O rupture easier and faster. Accordingly, the energy for the rupture of Si-O bonded interactions becomes as low as 22–29 kJ/mol, but the energy for forming the five-fold coordinated silicon atom is substantially higher at 63 kJ/mol in 3–21$G^*$ level and 88 kJ/mol (82 kJ/mol in enthalpy) in 6–311G(2d,p) level, which is consistent with the range of experimental values. This is the example to report the lowest energy barrier based on transition state theory for the $Q^3$Si → $Q^2$Si hydrolysis in a neutral surface condition.

The calculations in this study, suggest a new understanding of the mechanism whereby an alkali cation enhances the silica dissolution rate. This is based on increasing the coordination number of the silicon atom from four to five. The process of the Si-O hydrolysis occurs as the water molecule attacks the five-fold coordinated silicon through the intermediate of six-fold coordinated Si. The last rupture of $Q^3$Si to $Q^4$Si still remains for investigation.

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