Mechanism of Dissolution of Neutral Silica Surfaces: Including Effect of Self-Healing

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The common empirical idea that the dissolution of silica is controlled by the hydrolysis of the first Si−O−Si bond of Si surface species is checked against experimental activation energies by DFT (B3LYP) calculations using a polarized continuum model. The calculated energy barrier for the hydrolysis of a Si−O−Si bridge of a double-linked Si atom of β-cristobalite at the water−silica interface (29 kcal/mol) comes out to be higher than the measured activation energy of silica dissolution at the point of zero net proton charge of the surface (PZPC) by at least 7 kcal/mol. This discrepancy is significantly outside the estimated error bars of the calculations. Therefore, we propose a new mechanism, which is based on the assumption that the breakage of the first Si−O−Si bond is followed by the very fast reverse reaction of dehydroxylation of the formed Si−OH HO−Si defect. Because of this "self-healing" effect, the probability of both Si−O−Si bonds of the double-linked Si atoms being dissociated is very low, which explains the very small rate of dissolution of silica at PZPC. This mechanism also allows us to interpret the experimental fact that the preexponential factor of the reaction is extremely small. Within the new mechanism, the measured activation energy is associated with the hydrolysis of the last Si−O−Si bond of the Si atoms. Unlike the first Si−O−Si bond, the hydrolysis of the last bond is not hindered by the lattice resistance, which leads the theoretical activation energy (20 kcal/mol) to be in good agreement with experiment.

Introduction

The weathering and dissolution of the earth's crust silicate minerals have raised significant interest[1,2] because of the substantial increase in the rate of these processes during the past decades. This change in the geochemical equilibrium is mainly associated with the global acidification[1,2] caused by human activities. The fundamental mechanisms affecting the rate of dissolution of silicates should be understood for predicting the effects of these environmental changes.

It is commonly assumed[3−6] that the hydrolysis of Si−O−Si linkages is the key elementary step controlling the rate of silica dissolution. Although, in general, this hydrolysis depends on many chemical factors (pH, salt concentration, the nature of alkali cations, etc.), one particular case appears to be the most simple and appropriate for getting insight into the reaction mechanism with quantum chemical methods. This is the dissolution of silica at pH ∼ 3 corresponding to PZPC.[5] Under this condition, the contribution of the charged surface species $Si-O^-$ and $Si-OH_2^+$ to the reaction can be neglected, and the water molecules adjacent to the surface can be considered as the primary reagents for the reaction of breakage of Si−O−Si bridges:[5]

$$Si-O-Si + H_2O \rightarrow Si-OH\ HO-Si \qquad (1)$$

According to experimental studies, the activation energy for this reaction should be within the 16−22 kcal/mol range.[6−10] One can take this range of experimental values as reference data when studying the reaction mechanism with theoretical methods.

Recently we performed DFT calculations of the Si−O−Si hydrolysis at the (001) and (111) planes of β-cristobalite by a single water attack from the gas phase.[12] As distinct from the previous quantum chemical studies of the reaction,[10,13] our models included the steric constraints imposed by the solid matrix on the Si−O−Si linkage and its nearest surroundings. These calculations showed that the energy barrier ΔE_d for the dissociation of a Si−O−Si bond at a Si atom strongly depends on the connectivity of this atom to the solid; the estimated energies for the double-, triple-, and quadruple-linked Si species were 23, 33, and 49 kcal/mol, respectively. This effect is caused by the resistance of the lattice to the relaxation of the activated complex of the reaction: the larger the number of Si−O−Si bonds for a Si atom, the stronger the resistance of the solid to the hydrolysis of a Si−O−Si bond. Because of this effect, the dissolution should be dominated by the release of the Si atoms with the lowest connectivity. Therefore, excluding the case of dissolution of freshly ground silica powders with a significant concentration of surface defects,[12,14] the release of the double-linked Si atoms should mainly contribute to the experimental reaction rate. In line with the common assumption,[5] on the basis of these results one could also suggest that the dissociation of the first Si−O−Si bridge of these Si atoms should be the rate-determining step of the reaction.

In this work, we calculate the energy barrier for the dissociation of a first Si−O−Si bond of a double-linked Si atom of β-cristobalite for the case of the "uncharged" solid−liquid interface corresponding to PZPC. The calculations are performed at the DFT level within the approximation of a polarized

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continuum model. The energy barrier (29 kcal/mol) turns out to be larger than the observed activation energy by at least 7 kcal/mol. Our examination of the theoretical accuracy suggests that this discrepancy is considerably larger than the possible error of calculations. Therefore, we conclude that the hydrolysis of the first Si−O−Si bond of the Si species does not directly control the reaction rate and propose a new mechanism of silica dissolution. This mechanism is based on the assumption of the importance of the "self-healing" effect in the dissolution kinetics, namely, the very fast reverse reaction of dehydroxylation of the Si−OH HO−Si surface defects formed by reaction 1

$$\mathrm{Si{-}OH + HO{-}Si \rightarrow Si{-}O{-}Si + H_2O} \tag{2}$$

In these defects, the connectivity of the Si−OH groups to the lattice forces them to remain nearest neighbors, which leads to a high probability of reaction 2. This is analogous to the so-called cage effect for chemical reactions in solutions and dense media. The significance of the self-healing effect for the kinetics of dissolution of ≡Si−O−T≡ (T = Si and Al) bridges has been discussed earlier for the hydrothermal chemistry of zeolites.[15,16] The inclusion of the self-healing effect allows us not only to reach good agreement between the measured and theoretical activation energies but also to explain some important peculiarities of the dissolution kinetics.

Details of Calculations

DFT and MP2 calculations were performed with the Gaussian-94 package.[17] For the DFT calculations the hybrid B3LYP functional[18] was employed which is a parametrized combination of the Becke exchange functional,[19] the Lee, Yang, and Parr correlation functional,[20] and the exact Hartree−Fock exchange. The standard 6-31G(d), 6-311G(d,p), 6-311G(df,p), and 6-311G(2df,pd) basis sets were used. Corrections for the basis set superposition error (BSSE) were estimated by the counterpoise method.[21] Only a few relevant 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.[22,23] As is commonly accepted for silica and silica-containing oxides,[22,23] the "dangling" valences of the border Si atoms were saturated with H atoms. To mimic the structural restrictions imposed by the lattice, the position of the border SiH_3 groups were kept fixed in the geometry optimization. These positions were determined by the procedure described in ref 12.

The solvent effect was included with a self-consistent isodensity polarized continuum model (SCIPCM) by means of the Gaussian-94 SCRF=SCIPCM option.[18] These calculations were carried out without geometry optimization using the geometry optimized for the corresponding solid−gas models.

Because our cluster models are not fully optimized, they cannot be used for estimating zero-point corrections to the activation energies of the Si−O−Si dissolution and the Si−OH HO−Si dehydroxylation. In line with previous theoretical studies of the reaction,[10,13] we assume these corrections to be approximately equal to the corresponding values for the analogous gas-phase reaction:

$$\mathrm{(HO)_3SiOSi(OH)_3 + H_2O \rightleftarrows [(HO)_3SiOSi(OH)_3{\cdot}H_2O]_{transition\ state} \rightleftarrows 2Si(OH)_4} \tag{3}$$

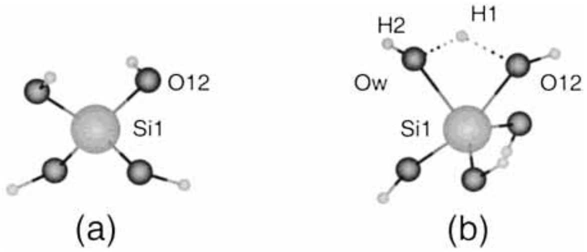

Figure 1. $Si(OH)_4$ (a) and the activated complex of the hydrolysis of one of its Si−O bond (b).

TABLE 1: Activation Energy, ΔE_d, of the Si−O Dissociation for $Si(OH)_4$ (kcal/mol)

method[a]	ΔE_d[b]
B3LYP/6-31G(d)	17.1 (15.4)
B3LYP/A	18.6 (16.9)
MP2/A//B3LYP/A	(17.8)
B3LYP/B	19.1 (17.3)
B3LYP/C	19.3 (17.4)

[a] Basis sets A, B, and C: the 6-31G(d) basis set on Si and the 6-311G(d,p) (A), the 6−311(df,p) (B), and the 6-311G(2df,pd) (C) basis sets on O and H. [b] ΔE_d without zero-point correction in parentheses.

When including the zero-point energy (E_{zp}) for the H_2O molecule in water, we also consider three restricted translational vibrations (110 cm^{-1} as the average of the stretching and bending vibrations of the O−H···O units involved in these motions[24]) and three librational vibrations (470, 550, and 775 cm^{-1} [24]):

$$E_{zp}(\mathrm{H_2O}) = 0.5hc(3 \times 110/2 + 470 + 550 + 780) = 2.7\ \mathrm{kcal/mol} \tag{4}$$

where h is the Planck constant and c is the speed of light. The energy corresponding to the translational vibrations is divided by 2 assuming that each of these vibrations is shared by two neighboring molecules.

Results and Discussion

The previous calculations of the reaction[10,12,13] were carried out with the 6-31G(d) basis set. However, the use of the same basis set for Si and O might result in a BSSE: the electrons on the negatively charged O atoms may tend to use the basis functions available on Si atoms to decrease their energy.[23] To examine this BSSE we calculated the dissolution of a Si−O bond of the $Si(OH)_4$ molecule (Figure 1) at the B3LYP level using the 6-31G(d) basis set and three combined basis sets A, B, and C with the 6-31G(d) basis set for Si and the 6-311G(d,p) (A), the 6-311G(df,p) (B), and the 6-311G(2df,pd) (C) basis sets for H and O. The activation energy was computed also at the MP2/A//B3LYP/A level. The calculated energies suggest (Table 1) that neither a further extension of the basis set on O atoms nor another method of inclusion of electron correlation should affect the B3LYP/A results significantly. Therefore, in the following consideration, we use the B3LYP method with basis set A.

Table 2 lists the calculated activation and reaction energies for the dissociation of the Si(2)−O−Si(3) bond (2 and 3 designate the number of Si−O−Si linkages to the surface) at the Si(2) atom by a single water attack from the gas phase (Figure 2). The models of the surface (**1a**), the activated complex (**2a**), and the Si−OH HO−Si defect (**3a**) were fully optimized except the positions of the border SiH_3 groups, which are used to ensure the structural restrictions imposed by the lattice. The calculated energy barrier equals 25 kcal/mol. The corresponding values for the $(HO)_3SiOSi(OH)_3$ molecule (Figure 3) are also presented in Table 2 for comparison. Table 3 reports selected bond lengths and bond angles of the models.

TABLE 2: Activation Energies[a] of Dissociation, ΔE_d, and Healing, ΔE_h, of the Si−O−Si Bridge (kcal/mol)[b]

	ΔE_d		ΔE_h	
model	gas phase	water ($\epsilon = 78$)	gas phase	water ($\epsilon = 78$)
$(HO)_3SiOSi(OH)_3$	17.5	20.5	13.3	19.1
1a	24.9	28.6	26.3	28.6
2a	18.0	19.9		

[a] Zero-point corrected. [b] Basis set A: the 6-31G(d) basis set on Si and the 6-311G(d,p) basis set on O and H.

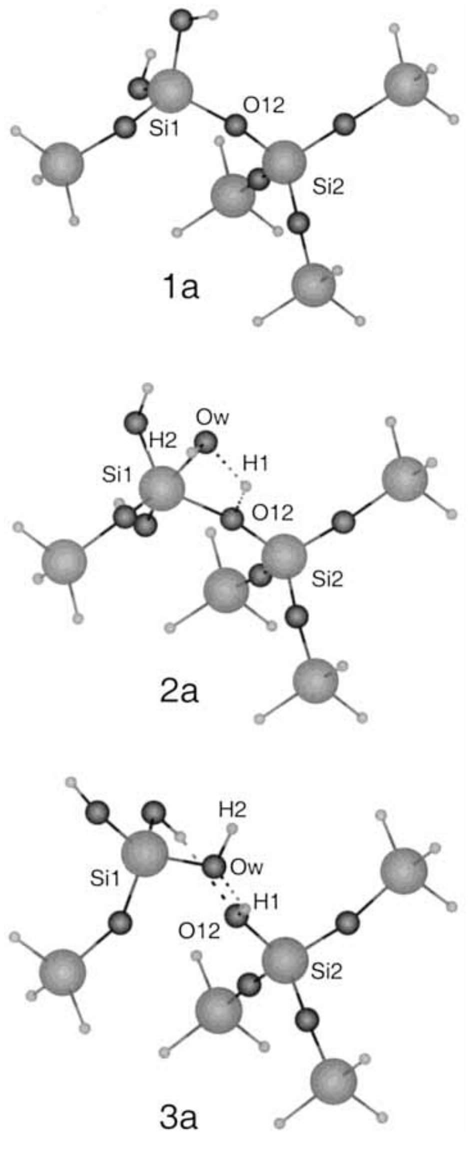

Figure 2. Cluster models of a siloxane bridge (**1a**), the activation complex of its hydrolysis (**2a**), and the hydrolyzed state of this bridge (**3a**) at the (111) β-cristobalite surface. For all models, the position of the border SiH_3 groups is identical and fixed modeling the structural constraints imposed by the lattice. In model **1a**, atom Si1 represents the double-linked species Si(2).

The inclusion of the solvent with the SCIPCM method increases the activation energy by 4 kcal/mol. This value results from the effect of the solvent on the "frozen nuclei" activation energy (6.4 kcal/mol) and the zero-point correction to the activation energy due to the restricted translational and librational vibrations of the H_2O molecule in water (−2.7 kcal/mol), which is not included when considering the solid−gas reaction. The effect of the solvent has been interpreted[10,23] in terms of the number of H-bonds formed by the subsystem Si−O−Si + H_2O with the surrounding water. Because in the activated complex the lone pairs of the attacking H_2O molecule are pointed out of the near-surface water, the reaction requires the breakage of the corresponding H-bonds of this molecule. This explanation suggests the estimated value of the solvent effect be physically reasonable. To note, simplified procedures of inclusion of the solvent[10] led to a similar increase of the energy barrier by 6−7 kcal/mol.

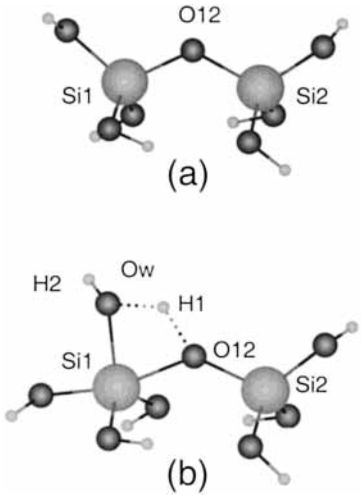

Figure 3. $(HO_3SiOSi(OH)_3$ (a) and the activated complex of the hydrolysis of its Si−O−Si bridge (b).

The resulting estimated barrier of 29 kcal/mol overestimates the experimental activation energy by at least 7 kcal/mol. No improvement of the basis set or the treatment of dynamical correlation should change this result (see the examination of the stability of calculated energies above). Therefore, we conclude that the experimental energy does not directly relate to the hydrolysis of the first Si−O−Si bond. Below we propose a new mechanism of the reaction.

The rate constants for the hydrolysis and the reverse reaction of healing of a Si(2)−O−Si(3) surface bridge

$$\mathrm{Si(2){-}O{-}Si(3)} + \mathrm{H_2O} \underset{k_h(1)}{\overset{k_d(2)}{\rightleftharpoons}} \mathrm{Si(1){-}OH\ HO{-}Si(2)} \quad (5)$$

can be expressed as

$$k_d(2) = \nu_d \exp\{-\Delta E_d(2)/kT\} \quad (6)$$

$$k_h(1) = \nu_h(1) \exp\{-\Delta E_h(1)/kT\} \quad (7)$$

where ν_d is the preexponential factor for the water attack onto a Si−O−Si bridge which is considered to be independent of the connectivity, $\nu_h(1)$ is the preexponential factor for the reaction of healing, $\Delta E_d(2)$ and $\Delta E_h(1)$ are the corresponding energy barriers. In the Si−OH HO−Si defect, the remaining connectivity of the Si atoms to the lattice forces the Si−OH groups to be nearest neighbors perfectly arranged for the reverse reaction of dehydroxylation. Therefore, we can take $\nu_h(1)$ to approximately equal the characteristic frequency of atomic vibrations of the lattice[15,16]

$$\nu_h(1) \sim 10^{13}\ \mathrm{s}^{-1} \quad (8)$$

In terms of the collision theory of chemical reactions[25]

$$\nu_d = Pz_d \quad (9)$$

TABLE 3: Selected Geometry Parameters (Bond Lengths in Angstroms and Bond Angles in Degrees)

model	Si1−O12	Si2−O12	Si1−Ow	O12−H1	O_w−H1	O_w−H2	Si1−O12−Si2
1a	1.63	1.63					153
2a	1.84	1.67	1.89	1.09	1.38	0.96	146
3a		1.64	1.67	0.98		0.97	
1b	1.64	1.64					149
2b	1.86	1.69	1.90	1.31	1.13	0.97	143
$Si(OH)_4$	1.65						
$Si(OH)_4 \cdot H_2O$	1.90		1.86	1.33	1.12		
$(HO)_3SiOSi(OH)_3$	1.65	1.65					137
$(HO)_3SiOSi(OH)_3 \cdot H_2O$	1.95	1.64	1.82	1.26	1.16	0.96	129

where P is the steric factor and z_d is the frequency of water attacks onto the Si−O−Si bridge. Each of these attacks is associated with the jump of a nearby H_2O molecule from the near-surface water toward the hydrophobic Si−O−Si bridge. Therefore, we can assume z_d to be equal to the intermolecular vibrational frequency of bulk water[24]

$$z_d \sim 10^{12}\ \mathrm{s}^{-1} \qquad (10)$$

Because $\Delta E_d(2) = \Delta E_h(1)$ (Table 2) and P is normally found to be several orders of magnitude smaller than 1,[25] we have from eqs 6−10 that

$$k_d(2)/k_h(1) \sim 10^{-1}P \ll 1 \qquad (11)$$

and we obtain $k_d(2)$ several orders of magnitude smaller than $k_h(1)$.

For $\tau_h(1) = 1/k_h$ and $\tau_d(2) = 1/k_d$, which are the characteristic lifetimes of the Si(1)−OH HO−Si(3) defect and the Si(2)−O-Si(3) bridge, respectively, this means that

$$\tau_h(1) \ll \tau_d(2) \qquad (12)$$

Inequality 12 represents a mathematical expression of the healing effect, implying that the healing immediately follows the dissolution with a very high probability.

Assuming that the rate-limiting step for the release of Si(2) species is the breakage of the last Si−O−Si bond (the diffusion of $Si(OH)_4$ away from the surface should be much faster[11]), the reaction rate is given by

$$k = k_d(1)p \qquad (13)$$

where

$$k_d(1) = \nu_d \exp\{-\Delta E_d(1)/kT\} \qquad (14)$$

is the rate constant for the dissociation of the Si−O−Si bond of single-connected Si(1) atoms, $\Delta E_d(1)$ being the related energy barrier, and

$$p = 2\tau_h(1)/(\tau_h(1) + \tau_d(2)) \cong \tau_h(1)/\tau_d(2) = k_d(2)/k_h(1) \ll 1 \qquad (15)$$

is the probability for one of two Si−O−Si bonds of a Si(2) atom to be hydrolyzed.

When using models **1b** and **2b** (Figure 4), for the solid−liquid interface, $\Delta E_d(1)$ equals 20 kcal/mol. $\Delta E_d(1)$ is smaller than $\Delta E_d(2)$ because the hydrolysis at the Si(1) atoms is not hindered by the lattice. Finally, from eqs 11 and 13−15 we have for the appearing activation energy ΔE_a of the reaction

$$\Delta E_a = \Delta E_d(1) + \Delta E_d(2) - \Delta E_h(1) = 20\ \mathrm{kcal/mol} \qquad (16)$$

which is in good agreement with experiment.

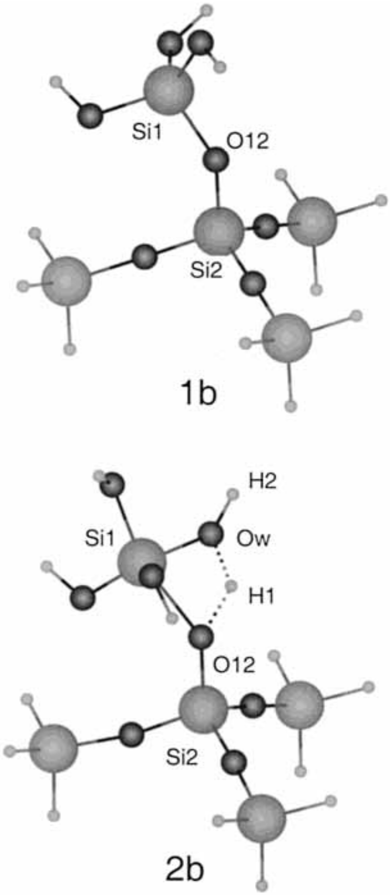

Figure 4. Cluster models of a Si−O−Si$(OH)_3$ surface bridge (**1b**) and the activation complex of its hydrolysis (**2b**) at the (111) β-cristobalite surface. For both models, the position of the border SiH_3 groups is identical and fixed modeling the structural constrains imposed by the lattice. In model **1b**, atom Si1 represents the single-linked species Si(1).

Summarizing, we propose that the release of the double-linked Si species follows the reaction scheme

$$\mathrm{Si(3){-}O{-}Si(2)} \underset{-\mathrm{H_2O}}{\overset{+\mathrm{H_2O}}{\rightleftarrows}} \mathrm{Si(2){-}OH\ HO{-}Si(1)} \xrightarrow{+\mathrm{H_2O}} \mathrm{Si(2){-}OH} + \mathrm{Si(OH)_4} \qquad (17)$$

Within this mechanism, the reaction rate is actually related to the release of the single-linked Si(1) species. Because, due to the self-healing effect, the dynamical equilibrium between the Si(3)−O−Si(2) bridges and the Si(2)−OH HO−Si(1) defects (reaction 5) is strongly shifted to the left, the concentration of the Si(1) is very small. This explains why, despite the relatively small activation energy, silica samples may remain stable in dissolution experiments over geological times.[26]

The new mechanism is also able to explain two interesting experimental facts. These facts and their explanation within the proposed mechanism are as follows:

1. At hydrothermal conditions, extremely rapid oxygen interchange takes place between the Si−O−Si bridges of zeolites and H_2O:[18,27,28]

$$\text{Si}-\text{O}-\text{Si} + \text{H}_2\text{O}^{18} \rightarrow \text{Si}-\text{OH HO}^{18}-\text{Si} \rightarrow \text{Si}-\text{O}^{18}-\text{Si} + \text{H}_2\text{O} \quad (18)$$

Although the breakage of the Si−O−Si bonds is very fast, the zeolite lattice remains unchanged at these conditions for years. This means that the probability for several Si−O−Si bonds at a Si atom being hydrolyzed is practically excluded. The self-healing effect appears to be the only plausible explanation of this fact.

2. Dove has developed[5] a general expression for the rate of silica dissolution by fitting the commonly accepted model of the $Si(OH)_4$ release to numerous independent measurements for pH 2−12 and 25−300 °C:

$$k = 10^{-4.6} T \exp\{-15.8/kT\}\theta_{\text{SiO}} + 10^{2.0} T \exp\{-19.8/kT\}\theta_{\text{SiO}^-} \quad (19)$$

where θ_{SiO} and θ_{SiO^-} are the fractions of Si−OH and $Si-O^-$ surface species, respectively. The first term corresponds to the discussed reaction at PZPC, and the second term accounts for the dissociation of the charged surface at high pH. One can note that the preexponential factor for the charged surface is larger by about 7 orders of magnitude compared to that of the neutral surface, which leads the rate of dissolution at high pH to be much larger compared to that of PZPC. As mentioned above, the small preexponential factor for the dissolution at PZPC is accounted for by the very small concentration of the Si(1) species (cf. eq 17). Because for basic solutions the proton exchange is the fastest chemical reaction,[5] at high pH, a significant fraction of the Si−OH HO−Si defects formed by the hydrolysis should undergo deprotonation. This deprotonation prevents the self-healing, which results in the strong increase of both the preexponential factor and the rate of the reaction.

These two facts can be regarded as additional experimental support for the proposed mechanism.

Conclusion

Our calculations suggest that the energy barrier for the dissolution of the first Si−O−Si bond of Si surface species of silica is larger than the experimental activation energy for the release of $Si(OH)_4$ by at least 7 kcal/mol. To explain the observed activation energy, we propose a new mechanism which is based on the assumption of very fast dehydroxylation of the Si−OH HO−Si defects formed by the hydrolysis of the first Si−O−Si bond of the Si atoms. Within this mechanism, the experimental activation energy is associated with the hydrolysis of the last Si−O−Si bond of the Si species. Because the dissolution of this bond is not hindered by the lattice resistance,[12] the theoretical activation energy is in good agreement with experiment.

Because of the effect of self-healing of the Si−OH HO−Si defects, the probability for all Si−O−Si bonds being dissociated is very low. This explains why the dissolution of silica at the point of zero net proton charge of the surface is so slow. Within the proposed mechanism, the significant increase of the dissolution rate at high pH is accounted for by the suppression of the healing effect by deprotonation of the Si−OH HO−Si defects.

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References and Notes

(1) Sundquist, E. T. *Science* **1993**, *259*, 934.

(2) Berner, R. A. *Geochim. Cosmochim. Acta* **1992**, *56*, 3225.

(3) Mast, M. A.; Drever, J. I. *Geochim. Cosmochim. Acta* **1987**, *51*, 2559.

(4) Casey, W. H.; Westrich, H. R.; Arnold, G. W. *Geochim. Cosmochim. Acta* **1988**, *52*, 2795.

(5) Dove, P. M. *Am. J. Sci.* **1994**, *294*, 665.

(6) Walther, J. V. *Am. J. Sci.* **1996**, *296*, 693.

(7) Knauss, K. G.; Wolery, T. J. *Geochim. Cosmochim. Acta* **1988**, *52*, 43.

(8) Brady, P. V.; Walther, J. V. *Chem. Geol*. **1990**, *82*, 253.

(9) Dove, P. M.; Crerar, D. A. *Geochim. Cosmochim. Acta* **1990**, *54*, 955.

(10) Xiao, Y.; Lasaga, A. *Geochim. Cosmochim. Acta* **1994**, *58*, 5379.

(11) Rimstidt, J. D.; Barnes, H. L. *Geochim. Cosmochim. Acta* **1983**, *44*, 1683.

(12) Pelmenschikov, A. G.; Strandh, H.; Pettersson, L. G. M.; Leszczynski, J. *J. Phys. Chem.* B **2000**, *104*, 5779.

(13) Xiao, Y.; Lasaga, A. *Geochim. Cosmochim. Acta* **1996**, *60*, 2283.

(14) Nickel. *Contrib. Sedimentol.* **1973**, *1*, 1.

(15) Pelmenschikov, A. G.; Zhidomirov, G. M.; Zamaraev, K. I. In *Zeolites: Facts, Figures, Future*; Jackobs, P. A., van Santen, R. A., Eds.; Elsevier Science Publisher: Amsterdam, The Netherlands, 1989.

(16) Pelmenschikov, A. G.; Paukshtis, E. A.; Edisherashvili, M. O.; Zhidomirov, G. M. *J. Phys. Chem.* **1992**, *96*, 7051.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(18) Frisch, M. A.; Frisch, A. E.; Foresman, J. B. *Gaussian 94 User's Reference*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(21) Boys, S. F.; Bernard, F. *Mol. Phys.* **1970**, *19*, 553.

(22) Zhidomirov, G. M.; Kazanski, V. B. *Adv. Chem.* **1986**, *34*, 131.

(23) Sauer, J.; Ugliengo, P.; Garrone, E.; Saunders, V. R. *Chem. Rev.* **1994**, *94*, 2095.

(24) Walrafen, G. E. In *The Physics and Physical Chemistry of Water*; Franks, F., Ed.; Plenum Press: New York, 1972.

(25) Atkins, P. W. *Physical Chemistry*, 4th ed.; Oxford University Press: New York, 1990.

(26) Tester, J. W.; Worley, W. G.; Robinson, B. A.; Grigsby, C. O.; Feerer, J. L. *Geochim. Cosmochim. Acta* **1994**, *58*, 2407.

(27) Antoshin, G. V.; Minachev, K. H.; Sevastjanov, E. N.; Kondratjev, D. A.; Newy, C. Z. *Adv. Chem. Ser.* **1971**, *101*, 514.

(28) Oblad, A. G.; Hinder, S. G.; Mills, G. A. *J. Am. Chem. Soc.* **1953**, *75*, 4096.