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Thermochemistry of silicic acid deprotonation: Comparison of gas-phase and solvated DFT calculations to experiment

J. SEFCIK¹ and W. A. GODDARD III^{2,*}¹Laboratorium für Technische Chemie, ETH Zürich, Universitätsstr. 6, CH-8092 Zürich, Switzerland²Materials and Process Simulation Center, Beckman Institute, 139-74, California Institute of Technology, Pasadena, CA 91125, USA

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Abstract—Theoretical approaches to the thermochemistry of silicate anions have so far focused on gas-phase molecular orbital and density functional theory (DFT) calculations. These calculations predict that in the presence of hydroxide ligands the most stable singly charged anion of the silicic acid H_4SiO_4 is the five-coordinated anion H_5SiO_5^- . However, experimental evidence from in situ nuclear magnetic resonance (NMR) experiments clearly shows that deprotonated silicic acid in alkaline aqueous solutions is four-coordinated, H_3SiO_4^- . We compare gas-phase and solvated DFT calculations of monomeric anions of silicic acid in order to assess solvent effects on the thermochemistry of silicic acid deprotonation. We show that appropriate inclusion of solvation in quantum chemical calculations is critical for correct prediction of coordination and thermochemistry of silicate anions in aqueous solutions. Multiply charged anions of silicic acid are found to be electronically unstable in the gas phase and thus it is not possible to use thermodynamic cycles involving these species in thermodynamic calculations. However, a high dielectric constant solvent is sufficient to stabilize these anions, and solvated calculations can be used to directly compute their thermodynamic quantities. When we include the zero point energy (ZPE) and statistical mechanics contributions to the Gibbs free energy, we obtain accurate free energies for successive deprotonations of silicic acid in aqueous solutions. Although the pentacoordinate hydroxoanion of silicon is more stable in the gas phase than the four-coordinated one (by 18 and 5 kcal/mol in the self-consistent field (SCF) energy and the Gibbs free energy, respectively), it is less stable by 5 kcal/mol in the Gibbs free energy when hydration effects are appropriately accounted for. Solvated DFT calculations, validated here by their accurate description of silicate anions in aqueous solutions, should lead to more reliable predictions of important geochemical quantities, such as surface acidities and detailed reaction coordinates for dissolution of minerals. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Silicate anions play an important role in processes of growth and dissolution of minerals and synthetic materials, such as zeolites and their siliceous analogs. Anions of silicic acid and of its oligomers are prevalent species in alkaline aqueous solutions of silicates at $\text{pH} > 10$ (Iler, 1979) from which zeolites are typically synthesized (Barrer, 1982). Even at $\text{pH} < 9$, where most of the soluble silica is in the form of neutral monomers and dimers, silicate anions play the role of reactive species in silicic acid condensation via nucleophilic substitution (Iler, 1979; Brinker and Scherer, 1990; Sefcik and McCormick, 1997a) at pH above the isoelectric point of reacting silanols ($\text{pH} = 2$ for surface silanols and $\text{pH} = 4$ to 5 for monomeric silicic acid).

Although there are reliable experimental data for the Gibbs free energy of the first two deprotonations of silicic acid in the aqueous phase (Sefcik and McCormick, 1997b), there are no further experimental thermochemical data for either gas-phase or solvated silicates to which theoretical calculations could be compared. Unavailable experimental data are then substituted by appropriate calculations. Numerous molecular orbital calculations at ever increasing levels of theory have been performed for neutral silicate oligomers. Silicic acid monomer and dimer

geometries, energetics, and vibrational spectra were studied in great detail (Teppen et al., 1994; Kubicki and Sykes, 1995). More recent calculations focused on neutral species up to octamers, mainly rings and cages, believed to play a role of intermediates in the synthesis of amorphous and crystalline silica solids (Moravetski et al., 1996; Lewis et al., 1997; Catlow et al., 1998; Tossell and Sahai, 2000). Most of these calculations did correspond to gas-phase conditions, although association energies for monomer or dimer with one or few water molecules have been calculated (Lasaga and Gibbs, 1990; Xiao and Lasaga, 1994; Moravetski et al., 1996). Catlow et al. (1998) estimated solvation energies of neutral oligomers using both a simple group contribution method for the hydrogen bonding and the COSMO model of the solvent continuum.

There were fewer studies of silicate anions, though. Interactions between H_4SiO_4 and the hydroxide anion were studied by semiempirical methods (Davis and Burggraf, 1988; Burggraf et al., 1992), and a stable pentacoordinate anion H_5SiO_5^- has been predicted. Gas-phase ab initio calculations predicted the same, and it has been argued that H_5SiO_5^- might be a stable silicate anion in alkaline aqueous solutions (Kubicki et al., 1993; Ermoshin et al., 1997) from which zeolites are crystallized. A gas-phase ab initio study by Xiao and Lasaga (1996) showed that four- and five-coordinated anions of the silicic acid dimer have similar potential energies. Geometry and energetics of the singly deprotonated silicic acid H_3SiO_4^- (De Almeida and O'Malley, 1992; Kubicki et al., 1995; Rustad et al., 2000) and

* Author to whom correspondence should be addressed (wag@wag.caltech.edu).

Table 1a. Standard Gibbs free energies and enthalpies of formation: molecules and ions.

Species	$\Delta_f H^\circ$ (kcal/mol)	$\Delta_f G^\circ$ (kcal/mol)	Reference
H ⁺ (g)	+367.17 (± 0.01)	+362.57 (± 0.01)	a
H ⁺ (aq)	0	0	conventional
OH ⁻ (g)	-34.23 (± 0.07)	-33.05 (± 0.07)	b
OH ⁻ (aq)	-54.97 (± 0.01)	-37.57 (± 0.01)	c
H ₂ O (g)	-57.80 (± 0.01)	-54.63 (± 0.01)	a
H ₂ O (l)	-68.32 (± 0.01)	-56.68 (± 0.01)	a
H ₃ O ⁺ (g)	138.9 (± 3.0)	145.0 (± 3.0)	a
H ₃ O ⁺ (aq)	-68.33 (± 0.02)	-56.69 (± 0.02)	using pK _w (T)

^a Chase et al., 1985.

^b Wagman et al., 1982.

^c Gurvich et al., 1989.

also the doubly charged anion (Tossell, 1991; Rustad et al., 2000) were studied in detail, but solvent effects were included only up to few explicit water molecules (Kubicki et al., 1993; Moravetski et al., 1996; Tossell and Sahai, 2000). Molecular dynamics studies of hydrated H₄SiO₄ and H₃SiO₄⁻ have also been carried out with various force fields (Rustad and Hay, 1995; Lewis et al., 1997).

There is both theoretical and experimental evidence of five-coordinate silicon in melts, glasses, and certain minerals (Xue et al., 1989; Kubicki and Lasaga, 1990; Stebbins, 1991; Poe et al., 1992; Angel et al., 1996) and in organometallic silicon compounds (Damrauer, 1988; Holmes, 1990; Chuit et al., 1993; Holmes 1996). Others (Liebau, 1984; Kubicki et al., 1993; Xiao and Lasaga, 1996) suggested that the formation of five-coordinate silicon species may play the key role in quartz dissolution at basic pH. Five-coordinate silicate anions can in fact be stabilized in aqueous solutions by bidentate organic ligands (Wong and Woollins, 1994; Tacke et al., 2000; Kinrade et al., 2001). However, ²⁹Si-NMR studies of alkaline aqueous silicate solutions unequivocally demonstrated that, even in very basic solutions, silicon in monomeric silicic acid is coordinated with four oxygens as H_{4-i}SiO₄ⁱ⁻, with degree of deprotonation *i* increasing with pH (Sefcik and McCormick, 1997b). Even though the five-coordinated silicate monomer anion H₅SiO₅⁻ seems to be stable in the gas phase (as indicated by theoretical calculations), and it certainly is a plausible metastable reaction intermediate in the aqueous phase or at a mineral surface, experimental evidence suggests that it is most likely not stable in a high dielectric constant solvent, such as water, where solvation energetics generally favors formation of smaller, more compact anions.

One of the important purposes of quantum mechanical computational studies on various silicate species is to understand the kinetics and mechanisms of mineral dissolution and growth, and the role played by these species in such processes. It is thus crucial to understand the utility of different computational methods in describing the energetics of geochemical reactants in their stable states as well as along the reaction coordinate (Xiao and Lasaga, 1996). To reconcile theoretical calculations with experiments, it is clearly desirable to include solvation effects in quantum mechanical calculations. In this paper we compare gas-phase and solvated density functional theory (DFT) calculations of monomeric anions of silicic acid to assess solvent effects on the thermochemistry of silicic acid deprotonation. We show that solvated DFT calculations are

capable to accurately describe silicate anions in aqueous solutions, as an initial step in validating this methodology for wider geochemical applications, such as calculation of mineral surface acidities and detailed reaction coordinates for growth and dissolution of minerals.

2. METHODS

2.1. Thermodynamic Standard States

Thermodynamic quantities, such as enthalpy or Gibbs free energy, should always be referred to specific reference states. In literature it is common to find variously defined thermodynamic quantities, which can be mutually compared only if the corresponding reference states are taken into account. Let us start with standard thermodynamic quantities customarily denoted by ^o (Tissandier et al., 1998). Thermodynamic quantities of formation from elements in their standard states are tabulated in standard compilations (Wagman et al., 1982; Chase et al., 1985). Standard states used in these compilations are as follows: (1) for the gas phase, the ideal gas at temperature 298.15 K and pressure 0.1 MPa; (2) for bulk water, pure liquid at temperature 298.15 K and pressure 0.1 MPa; (3) for solutes different from the solvent, ideal solution at unit molality at temperature 298.15 K and pressure 0.1 MPa. In addition, the scale of standard thermodynamic quantities of formation for ions in water is adjusted by a constant so that the standard Gibbs free energy and enthalpy of formation of the hydrogen cation (proton) in water is set to zero. This convention simply sidesteps the problem of exact determination of the hydration free energy and enthalpy for proton, data for which were apparently judged not to be sufficiently accurate. We will also address this point shortly. In some older literature on hydration thermodynamics (Friedman and Krishnan, 1973), a different standard state for the gas phase is used: (4) 1 mol/L ideal gas at temperature 298.15 K. One can easily calculate the free energy difference going from the standard state (4) to the standard state (3). It is the Gibbs free energy of isothermal, reversible expansion from density of 1 mol/0.001 m³ with the corresponding pressure 2.479 MPa to the standard pressure 0.1 MPa, which is easy to calculate for the ideal gas (Levine, 1988): $\Delta G = -1.90$ kcal/mol at 298.15 K. Therefore we can relate the Gibbs free energies of formation ΔG_f^o and ΔG_f^* , corresponding to the respective standard states (3) and (4), as: $\Delta G_f^o = \Delta G_f^* + 1.9$ kcal/mol. We list standard Gibbs free energy and enthalpy of formation for water and its dissociation products in Table 1 (using standard states as indicated). Note that it is not possible to dissect the sum of Gibbs free energies of hydration of proton and of hydroxide anion into its respective components by using solely the tabulated standard thermodynamic quantities of formation.

A range of values for the standard Gibbs free energy of proton hydration has been suggested (-250 to -265 kcal/mol, see Friedman and Krishnan, 1973; Grunwald and Steel, 1996). On one end of the range, the value of $\Delta G_h^o(\text{H}^+) = -252.4 (\pm 1.4)$ kcal/mol is quoted in widely used compilations of hydration free energies of ions (Marcus, 1991, 1994). This is rather far from more recent estimates (-260 to -264 kcal/mol, see below) and it is unlikely to be correct (see also discussion in Tawa et al., 1998). Experimental measurements of the

Table 1b. Standard Gibbs free energies and enthalpies: processes.

Process	ΔH° (kcal/mol)	ΔG° (kcal/mol)	ΔG^* (kcal/mol)
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ (g)	+390.8 (± 0.1)	+384.2 (± 0.1)	+386.1 (± 0.1)
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ (aq)	13.3	19.1	a
$\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$ (g)	+220 (± 3)	+221 (± 3)	+221 (± 3)
$\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$ (aq)	13.3	19.1	a
H_2O hydration	-10.52 (± 0.02)	-2.05 (± 0.02)	-6.324 (b)
$\text{H}^+ + \text{OH}^-$ hydration	-387.9 (± 0.1)	-367.1 (± 0.1)	-370.9 (± 0.3)
$\text{H}_3\text{O}^+ + \text{OH}^-$ hydration	-228 (± 3)	-206 (± 3)	-210 (± 3)

^a Definition not meaningful; imposes the standard state for liquid water as: 1 molar solution in itself.

^b Ben-Naim and Marcus, 1984.

standard hydrogen electrode potential indicated a value around $\Delta G_{\text{h}}^\circ(\text{H}^+) = -259.8$ (± 1.0) kcal/mol (Lim et al., 1991). Recently, quantum mechanical methods were used to calculate the Gibbs free energy of proton hydration (Tawa et al., 1998). The first hydration shell was treated explicitly by including up to 6 water molecules with the proton, embedded in a dielectric continuum. The calculated free energy decreased dramatically for up to 4 explicit water molecules, whereas for 4 to 6 molecules it stayed at a constant value $\Delta G_{\text{h}}^\circ(\text{H}^+) = -262.2$ kcal/mol. To get the standard Gibbs free energy of proton hydration, one has to add 1.9 kcal/mol [free energy difference going from the standard state (3) to the standard state (4)], so that the corresponding value is $\Delta G_{\text{h}}^\circ(\text{H}^+) = -260.3$ kcal/mol. The standard enthalpy and Gibbs free energy of proton hydration was recently also determined from cluster-ion solvation data using no extra thermodynamic assumptions (Tissandier et al., 1998). These authors suggest $\Delta G_{\text{h}}^\circ(\text{H}^+) = -264.0$ (± 0.1) kcal/mol.

The standard Gibbs free energy of hydration of the hydroxide anions $\Delta G_{\text{h}}^\circ(\text{OH}^-)$ can be determined when the corresponding quantity for $\Delta G_{\text{h}}^\circ(\text{H}^+)$ is known, because $\Delta G_{\text{h}}^\circ(\text{H}^+ + \text{OH}^-) = -367.1$ kcal/mol (Table 1). Using the (questionable) high end value $\Delta G_{\text{h}}^\circ(\text{H}^+) = -252.4$ kcal/mol, we get $\Delta G_{\text{h}}^\circ(\text{OH}^-) = -114.6$ kcal/mol, although the value printed in the book by Marcus is $\Delta G_{\text{h}}^\circ(\text{OH}^-) = -439$ kJ/mol (-105 kcal/mol) (Marcus, 1985). This might be a typographical error, which, however, propagated to both subsequent compilations (Marcus, 1991, 1994) and it is commonly cited and used. Moreover, Marcus also quotes the value of $\Delta G_{\text{h}}^\circ(\text{H}^+ + \text{OH}^-) = -369.3$ kcal/mol (-1545.0 kJ/mol in Table 5.10 (in Marcus, 1985) under conventional standard Gibbs free energy column. The source quoted for this number is his other book (Marcus, 1977), but there we did not find any explanation for why this value differs by ~ 2.2 kcal/mol from the one above calculated using standard compilations (Wagman et al., 1982; Chase et al., 1985). Thus, it is probably also an error. We believe that $\Delta G_{\text{h}}^\circ(\text{H}^+ + \text{OH}^-) = -367.1$ kcal/mol should be used, from which one can calculate the standard Gibbs free energy of hydration of OH^- according to what value of $\Delta G_{\text{h}}^\circ(\text{H}^+)$ one chooses. For example, if we choose $\Delta G_{\text{h}}^\circ(\text{H}^+) = -264.0$ kcal/mol (Tissandier et al., 1998), then $\Delta G_{\text{h}}^\circ(\text{OH}^-) = -103$ kcal/mol.

2.2. Computational Methods

We calculated energies and vibrational frequencies of silicate anions using DFT, which has been a reliable technique for calculations of molecular properties and energetics (Parr and Yang, 1989; Labanowski and Andzelm, 1991). Our calculations were performed with the Jaguar software package (Jaguar, 1998) using the B3LYP functional with the 6-31G** basis set (with and without diffuse functions). For comparison, we also performed gas-phase geometry optimizations using Hartree-Fock (HF) and local MP2 (LMP2) methods with a wider choice of basis sets. DFT calculations for each molecule were executed in the following order: (1) gas-phase geometry optimization without symmetry constraints; (2) harmonic frequency calculations to verify energy minima and to calculate zero point energies (ZPE) and statistical mechanics contributions to enthalpy (H_{298}) and free energy (G_{298}) corresponding to vibrational, rotational, and translational degrees of freedom at 298 K; (3) solvated geometry optimization without symmetry constraints; (4) solvated harmonic frequency calculations to

verify energy minima and to calculate ZPE and thermodynamic contributions at 298 K.

Solvation free energy can then be calculated as a difference between the self-consistent field (SCF) energies from gas-phase (1) and solvated (3) calculations. Solvated calculations were executed with a self-consistent scheme which cycles through quantum mechanical calculations in the solvent reaction field and continuum electrostatic calculations using polarized solute charges (Tannor et al., 1994). At each iteration a wavefunction is calculated in the field of the solvent and then the charges (based on electrostatic potential) are used to calculate the new reaction field. This process is repeated until convergence is reached. This method accounts for detailed molecular shape of a solvated molecule, which is determined by the van der Waals radius plus the solvent radius R_o around each atom. We assumed $\epsilon = 80$ and $R_o = 0.14$ nm based on using water as solvent. Solvation atomic radii were originally adjusted (Tannor et al., 1994) to accurately reproduce hydration free energies of neutral organics, and we used these radii as a default set: $r(\text{O}) = 0.160$ nm, $r(\text{H}) = 0.115$ nm, $r(\text{Si}) = 0.215$ nm. We also optimized solvation atomic radii of oxygen and hydrogen to better reproduce available experimental data on hydration free energies of water ions.

Solvation free energy calculated by usual methods of embedding a solute molecule into a solvent continuum (irrespective of actual model for the evaluation of solute-solvent interactions) corresponds to a transfer of a solute molecule from a fixed position (of its center of mass) in gas phase to a fixed position (of its center of mass) in solvent at a given temperature and pressure. This is exactly the Gibbs free energy of hydration denoted by ΔG_{h}^* , as defined by Ben-Naim and Marcus (1984). It was shown (Ben-Naim, 1978) that the same Gibbs free energy of hydration ΔG_{h}^* applies to a transfer of a solute molecule between gas phase and solvent, where solute concentration (density) is the same in both phases (with the infinite dilution a special case). For example, when the solute concentration is 1 mol/L in both phases, the Gibbs free energy of hydration ΔG_{h}^* corresponds to a transfer from an ideal gas phase of solute at 2.479 MPa [standard state (4)] to an ideal 1 mol/L aqueous solution [standard state (1)]. In contrast, the standard Gibbs free energy of hydration $\Delta G_{\text{h}}^\circ$ corresponds to a transfer from an ideal gas phase of solute at 0.1 MPa [standard state (3)] to an ideal 1 mol/L aqueous solution [standard state (1)]—except when water is the solute. As we showed above, the Gibbs free energy difference going from standard state (4) to standard state (3) is -1.90 kcal/mol, i.e., the standard state (3) is lower on the free energy scale than standard state (4). At temperature 298.15 K, the corresponding relation for hydration free energies of all solutes except water is thus $\Delta G_{\text{h}}^\circ = \Delta G_{\text{h}}^* + 1.9$ kcal/mol. When water is the solute, the standard Gibbs free energy of hydration corresponds to a transfer from an ideal gas phase of solute to a pure liquid water, and hence the above relation is not applicable. The Gibbs free energy of hydration ΔG_{h}^* for water was evaluated from vapor pressure data (Ben-Naim and Marcus, 1984), and at temperature 298 K the value is -6.32 kcal/mol. Gibbs free energies of hydration for neutral solutes can be conveniently calculated from solubility data, at least for small solutes, and extensive tabulations are available (Cabani et al., 1981).

Table 2. Gas-phase SCF energy of deprotonation (kcal/mol). Comparison of HF, LMP2 and DFT calculation results with various basis sets.

Process	$\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$\text{H}_4\text{SiO}_4 = \text{H}^+ + \text{H}_3\text{SiO}_4^-$
HF, 6-31G**	253.7	433.6	376.8
LMP2, 6-31G**	255.7	434.9	369.9
DFT, 6-31G**	255.7	435.1	370.1
DFT, cc-VTZ(-f)	245.7	419.8	365.0
HF, 6-31G**++	230.4	406.1	367.7
HF, cc-VTZ(-f)++	231.4	406.6	369.9
LMP2, 6-31G**++	223.0	395.4	355.8
LMP2, cc-VTZ(-f)++	221.2	393.5	357.0
DFT, cc-VTZ(-f)++	224.2	394.9	359.1
DFT, 6-31G**++	223.7	395.5	356.6
DFT, 6-31G**++//6-31G**	223.6	395.5	358.1
DFT, 6-31G**+	223.9	395.7	357.2
DFT, 6-31G**+//6-31G**	223.8	395.7	356.7
Experiment (from Table 1b)	223 (± 3.6)	398 (± 1)	—

3. RESULTS AND DISCUSSION

3.1. Gas-phase Calculations

First we calculated gas-phase SCF energies of deprotonation for water and silicic acid computed by various combinations of calculation methods (HF, LMP2, DFT) and basis sets (6-31G**, cc-VTZ(-f); with and without diffuse functions). Diffuse functions are denoted by + or ++ for heavy and all atoms, respectively, and their use has been recommended to obtain more accurate deprotonation energies (Hehre et al., 1986). We assess accuracy of a range of computational choices by comparing calculated SCF energies for water deprotonation to experimental gas-phase values (from Table 1, corrected for 0 K and ZPE). Results are summarized in Table 2. When basis sets without diffuse functions are used, deprotonation energy of water is overpredicted, regardless of the method, by 20 to 40 kcal/mol. When diffuse functions are used with the HF method, the deprotonation energy is overpredicted by 7 to 9 kcal/mol. Errors between -2.3 and -3.1 kcal/mol (compared to the experimental uncertainty ± 1 kcal/mol for $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$, while there is experimental uncertainty ± 3.6 kcal/mol for $\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$) are obtained with the DFT method and basis sets including diffuse functions. The deprotonation energies calculated using various basis sets are within

the range of 0.8 and 2.5 kcal/mol for water and silicic acid, respectively. We note that very accurate and costly calculation using G2 and CBS-4 methods (Rustad et al., 2000) yielded deprotonation energy for silicic acid ~ 5 kcal/mol lower than DFT calculations with the B3LYP functional. For the computational accuracy and cost considered here, there is no significant difference in accuracy between combinations of computational choices listed in the lower part of Table 2, so that it is most economical to use the fastest option. That is the last one listed in Table 2, i.e., DFT geometry optimization and thermodynamic calculations with the 6-31G** basis set followed by the DFT calculation of the SCF energy with the 6-31G**+ basis set. We used this method to obtain all results reported further, unless indicated otherwise.

Gas-phase geometry optimization resulted in the structure of silicic acid H_4SiO_4 possessing the S_4 symmetry in agreement with previous computational studies (De Almeida and O'Malley, 1992; Kubicki et al., 1993; Teppen et al., 1994; Xiao and Lasaga, 1994; Catlow et al., 1998; Pereira et al., 1999). Geometry was also optimized for silicic acid anions, H_3SiO_4^- , H_5SiO_5^- , $\text{H}_2\text{SiO}_4^{2-}$, HSiO_4^{3-} , SiO_4^{4-} , and for neutral, protonated and deprotonated water. Resulting symmetries and SCF energies are listed in Table 3. For electronically stable species, we also report calculated ZPE and statistical mechanics contri-

Table 3. Energetics in gas phase.

Species	Resulting symmetry	SCFE (hartree)	ZPE (kcal/mol)	H_{298} (kcal/mol)	G_{298} (kcal/mol)
H_4SiO_4	S_4	-593.0183	36.1	5.2	-18.6
H_3SiO_4^-	C_1	-592.4498	28.7	5.0	-18.4
$\text{H}_2\text{SiO}_4^{2-}$	C_2	(-591.6969) ^a	—	—	—
HSiO_4^{3-}	C_8	(-590.7605) ^a	—	—	—
SiO_4^{4-}	T_d	(-589.6645) ^a	—	—	—
H_5SiO_5^- (A)	C_1	-668.9021	46.1	5.6	-19.5
H_5SiO_5^- (B)	C_1	-668.9129	46.0	5.7	-19.8
H_2O	C_{2v}	-76.4339	13.4	2.4	-11.1
H_3O^+	C_{3v}	-76.7078	21.6	2.4	-11.4
OH^-	$C_{\infty v}$	-75.8033	5.0	2.1	-10.2
H^+	atomic	0	0	1.5	-6.3

^a Electronically unstable species.

Table 4. Energetics in aqueous solution calculated with default atomic radii.

Species	Resulting symmetry	SCFE (hartree)	ΔG_h^* (kcal/mol)	ZPE (kcal/mol)	H_{298} (kcal/mol)	G_{298} (kcal/mol)
H_4SiO_4	S_4	-593.0456	-17.1	35.5 ^a	5.3 ^a	-18.9 ^a
$H_3SiO_4^-$	C_1	-592.5791	-81.1	28.5	4.9	-19.0
$H_2SiO_4^{2-}$	C_1	-592.0978	—	22.0	4.3	-18.3
$HSiO_4^{3-}$	C_s	-591.6040	—	15.1	3.9	-17.9
SiO_4^{4-}	T_d	-591.1065	—	8.3	3.4	-16.0
$H_5SiO_5^-$ (A)	C_1	-669.0271	-78.4	45.4	5.7	-19.6
$H_5SiO_5^-$ (B)	C_1	-669.0271	-71.7	45.1	5.8	-19.8
H_2O	C_{2v}	-76.4477	-8.7	13.3	2.4	-11.1
H_3O^+	C_{3v}	-76.8647	-98.5	22.4	2.4	-11.4
OH^-	$C_{\infty v}$	-75.9606	-98.7	5.4	2.1	-10.2
H^+	atomic	—	-272.2 ^c	0	1.5 ^b	-6.3 ^b

^a 6-31G**++

^b Gas-phase values.

^c Using $\Delta G_h^*(H^+ + OH^-) = -370.9$ kcal/mol (Table 1b).

butions (Hehre et al., 1986) to enthalpy (H_{298}) and free energy (G_{298}) in Table 3. Energetics of any chemical or conformational transformation including species listed in Table 3 can now be consistently calculated by summing appropriate energetic contributions. For example, the Gibbs free energy of the gas-phase conformational change $H_5SiO_5^-$ (A) = $H_5SiO_5^-$ (B) is calculated as

$$\begin{aligned} & (\text{SCFE} + \text{ZPE} + G_{298})(B) - (\text{SCFE} + \text{ZPE} + G_{298})(A) \\ &= (\text{SCFE}(B) - \text{SCFE}(A)) + (\text{ZPE}(B) - \text{ZPE}(A)) + (G_{298}(B) \\ & - G_{298}(A)) = (-668.9129 + 668.9021) \times 627.51 \\ & + (46.0 - 46.1) + (-19.8 + 19.5) = -6.8 (\Delta \text{SCFE}) \\ & - 0.1 (\Delta \text{ZPE}) - 0.3 (\Delta G_{298}) = -7.2 \text{ kcal/mol}, \end{aligned}$$

where 627.51 is the unit conversion factor from hartree to kcal/mol. The two stable conformations A and B of the five-coordinated silicate anion $H_5SiO_5^-$ differ by 7.2 kcal/mol in terms of the gas-phase Gibbs free energy due to an intramolecular hydrogen bond in the conformer B. Similarly, at least two stable conformations with different patterns of intramolecular hydrogen bonding were observed for the silicate dimer $H_6Si_2O_7$ (Teppen et al., 1994). Near-degenerate conformers of $H_3SiO_4^-$ were also studied previously (De Almeida and O'Malley, 1992).

Only singly charged anions were found to be electronically stable in the gas phase, whereas for doubly and higher charged species, $H_2SiO_4^{2-}$, $HSiO_4^{3-}$, SiO_4^{4-} , we calculated negative adiabatic ionization potentials (-77, -220, -362 kcal/mol, respectively, with the 6-31G** basis set). This observation is in agreement with recent calculations indicating that small multiply charged anions tend to be electronically unstable in the gas phase (Stefanovich et al. 1998). When certain species are unstable in the gas phase, it is clearly not possible to define solvation free energies even when these species are stable in solvated conditions. This implies that for processes involving such species it is not possible to use thermodynamic cycles using pathways going through the gas phase, as one might want to do for theoretical acidity calculations, for example. However, one can avoid using a thermodynamic cycle by directly calculating thermodynamic quantities of interest using solvated quantum mechanical calculations, as we show below.

3.2. Aqueous-phase Calculations

Geometry was optimized in solvent for the same species as in the gas-phase calculations reported above. Resulting symmetries, SCF energies (these also include solvation free energy ΔG_s^*), and thermodynamic values are listed in Table 4 for default values of solvation atomic radii [$r(O) = 0.160$ nm, $r(H) = 0.115$ nm, $r(Si) = 0.215$ nm]. All species were found to be electronically stable in aqueous phase. Note that ZPE and statistical mechanics contributions to enthalpy (H_{298}) and free energy (G_{298}) are all within 1 kcal/mol (often within 0.2 kcal/mol) of their gas-phase values. Calculated geometries and vibrational frequencies of silicate species for both gas-phase and aqueous calculations are reported in Tables 5 and 6.

3.2.1. New atomic radii for solvated calculations

Calculated solvation free energies should be matched against the experimental data (Table 1b) to validate our computational method and, if necessary, to fine-tune available parameters. The embedding of quantum mechanical wavefunction in the polarizable solvent continuum requires specification of cavity boundaries in the continuum, determined by appropriately chosen solvation atomic radii. Atomic radii that were originally chosen (Tannor et al., 1994) provide good performance for calculations of neutral solutes, and we use them as our starting point, keeping in mind that fine-tuning of solvation atomic radii is tied to the specific quantum chemical method chosen. From Table 4 we get the following comparison with experimental data: (a) hydration free energy of water $\Delta G_h^*(H_2O) = -8.7$ kcal/mol, compared to the experimental value of -6.3 kcal/mol; (b) sum of hydration free energies $\Delta G_h^*(H_3O^+ + OH^-) = -197.2$ kcal/mol, compared to the experimental value of -210 (± 3) kcal/mol. We can also calculate the hydration free energy of proton, subtracting the calculated hydration free energy of hydroxide anion $\Delta G_h^*(OH^-) = -98.7$ kcal/mol from the experimental value of $\Delta G_h^*(H^+ + OH^-) = -370.9$ (± 0.1) kcal/mol: $\Delta G_h^*(H^+) = -272.2$ kcal/mol, i.e., $\Delta G_h^o(H^+) = -270.3$ kcal/mol. This seems to be rather high with respect to the range of recently suggested values from -260 to -264 kcal/mol (see above). From these comparisons, it seems that the hydration

Table 5. Geometry of monomeric silicates: comparison of solvated and gas-phase calculations.

Molecule/Symmetry	d(Si-O) (Angstrom)	d(O-H) (Angstrom)	<(Si-O-H)	<(O-Si-O)	<(O-Si-O ⁻)	<(O ⁻ -Si-O ⁻)
H ₄ SiO ₄ /S ₄	1.647 (1.648)	0.969 (0.964)	115.8 (114.7)	107.8 (106.3) 112.9 (116.0)	—	—
H ₃ SiO ₄ /S ₄ (6-31G**++)	1.652 (1.652)	0.970 (0.965)	118.0 (116.8)	109.6 (106.3) 109.2 (115.9)	—	—
H ₃ SiO ₄ ⁻ /C ₁	1.688 (1.718)	0.967 (0.965)	111.8 (102.5)	100.0 (99.4)	114.5 (112.2)	—
	1.686 (1.701)	0.966 (0.965)	110.6 (103.8)	101.5 (101.6)	115.1 (113.6)	
	1.684 (1.699)	0.968 (0.965)	112.5 (105.3)	106.3 (107.2)	117.4 (121.0)	
	1.566 (1.562)	—	—	—	—	
H ₂ SiO ₄ ²⁻ /C ₁	1.730	0.967	108.0	97.6	107.6	119.2
	1.729	0.965	106.2		108.5	
	1.592	—	—		110.7	
	1.591	—	—		111.2	
HSiO ₄ ³⁻ /C _s	1.781	0.966	96.4	—	100.3	114.2
	1.622	—	—		106.2	114.1
	1.618	—	—		—	—
SiO ₄ ⁴⁻ /T _d	1.652	—	—	—	—	109.5
H ₅ SiO ₅ ⁻ (A)/C ₁	1.785 (1.824)	0.967 (0.966)	109.9 (106.1)	90 ± 2	—	—
	1.768 (1.767)	0.965 (0.936)	108.7 (104.8)	(90 ± 2)		
	1.719 (1.737)	0.967 (0.965)	107.3 (103.1)	120 ± 2		
	1.713 (1.716)	0.967 (0.966)	107.1 (103.1)	(120 ± 2)		
	1.709 (1.706)	0.967 (0.966)	105.2 (101.1)	179.4 (177.7)		
H ₅ SiO ₅ ⁻ (B)/C ₁	1.781 (1.821)	0.965 (0.964)	109.9 (104.2)	90 ± 2	—	—
	1.770 (1.764)	0.965 (0.933)	108.7 (105.2)	(90 ± 3)		
	1.717 (1.725)	0.968 (0.966)	105.6 (102.1)	120 ± 2		
	1.712 (1.725)	0.967 (0.966)	108.7 (102.2)	(120 ± 2)		
	1.710 (1.706)	0.967 (0.967)	106.1 (102.1)	178.7 (176.3)		

Gas-phase results in parentheses.

free energies of both OH⁻ and H₃O⁺ are underpredicted (hydration less favorable) by ~5 to 10 kcal/mol each, when using the default values for solvation atomic radii. To achieve more favorable hydration, one ought to decrease solvation atomic radii r(O) and r(H). Note that this leads to even more favorable hydration of water, so that an optimum set of values can be found. Because it was not our objective to describe solvation of water by itself, we proceeded to improve calculated values of ΔG_h^{*}(H₃O⁺ + OH⁻) and keeping ΔG_h^{*}(H₂O) reasonable while adjusting solvation atomic radii r(O) and r(H). This led to a new set of solvation atomic radii: r^{new}(O) = 1.5, r^{new}(H) = 1.1. The corresponding SCF energies and hydration free energies are listed in Table 7, with much improved comparison with experimental data for ions. We get ΔG_h^{*}(H₃O⁺ + OH⁻) = -206.6 kcal/mol, compared to the experimental value of -210 (±3) kcal/mol). Also, the calculated value of the hydration free energy of proton, ΔG_h^{*}(H⁺) = -265.2 kcal/mol, compares well to the range of recently suggested values, -260 to -264 kcal/mol.

3.2.2. Successive deprotonations of silicic acid

Now we proceed to calculate free energy of silicic acid deprotonation in aqueous solutions using the optimized values of solvation atomic radii for oxygen and hydrogen. We note

that the atomic radius of silicon was not changed, so that the optimized solvation atomic radii for oxygen and hydrogen are not specific for silicates. Various contributions to free energy of deprotonation are detailed in Table 8. Note that SCF energies include hydration free energy ΔG_h^{*}. We used ΔG_h^{*}(H⁺) = -267.1 kcal/mol from Table 7. Our calculations correctly predict the trend that further deprotonation becomes several kcal/mol more difficult with increasing charge on the anion. Moreover, we match the Gibbs free energy of the aqueous deprotonation of H₄SiO₄ very accurately, underpredicting by -1.1 kcal. We note that this value was overpredicted by 4.6 kcal/mol in a molecular dynamics study with explicit water molecules (Rustad and Hay, 1995). For the second deprotonation, we get the Gibbs free energy of the aqueous deprotonation of H₃SiO₄⁻ overpredicted by 3.3 kcal/mol. Calculations for subsequent deprotonations can be compared to values estimated from linear extrapolations of pK values (Sefcik and McCormick, 1997b), and the calculated free energies overpredict those estimates by 1.6 and 5.1 kcal/mol for H₂SiO₄²⁻ and HSiO₄³⁻, respectively. Notice that these errors are of a magnitude to be reasonably expected in gas-phase calculations, and thus their source cannot be simply assigned to either the electronic wavefunction or the solvent effects, because these are coupled during geometry optimization and energy evaluation.

Table 6. Harmonic frequencies of monomeric silicates in gas phase and in solution.

Molecule/Symmetry	Gas/Solution	Frequencies (cm ⁻¹)
H ₄ SiO ₄ /S ₄	G	174, 188, 234, 234, 267, 345, 361, 361, 402, 759, 846, 851, 851, 856, 944, 1014, 1014, 3884, 3884, 3885, 3886
H ₄ SiO ₄ /S ₄	G	174, 196, 281, 295, 296, 331, 336, 357, 385, 746, 817, 817, 825, 827, 922, 977, 977, 3904, 3904, 3907, 3918
	S	131, 132, 192, 261, 288, 369, 369, 398, 403, 752, 810, 810, 827, 908, 908, 911, 999, 3840, 3843, 3843, 3856
H ₃ SiO ₄ ⁻ /C ₁	G	6, 177, 239, 304, 335, 361, 379, 418, 707, 782, 824, 917, 955, 966, 1173, 3844, 3857, 3863
	S	80, 209, 253, 282, 312, 357, 388, 402, 741, 791, 807, 861, 897, 942, 1137, 3822, 3837, 3846
H ₂ SiO ₄ ²⁻ /C ₁	S	155, 232, 295, 326, 415, 435, 506, 696, 718, 877, 918, 972, 1126, 3826, 3858
HSiO ₄ ³⁻ /C _s	S	237, 285, 333, 428, 510, 527, 651, 823, 861, 1024, 1040, 3829
SiO ₄ ⁴⁻ /T _d	S	345, 345, 511, 512, 513, 780, 929, 929, 929
H ₅ SiO ₅ ⁻ (A)/C ₁	G	135, 200, 234, 280, 361, 380, 388, 409, 410, 474, 559, 580, 622, 657, 684, 803, 828, 931, 985, 1010, 1040, 1112, 3808, 3823, 3824, 3828, 3865
	S	125, 165, 233, 282, 369, 389, 396, 413, 426, 497, 518, 527, 589, 673, 684, 793, 799, 888, 918, 967, 968, 1031, 3807, 3812, 3823, 3826, 3853
H ₅ SiO ₅ ⁻ (B)/C ₁	G	88, 166, 224, 265, 355, 373, 390, 402, 406, 495, 555, 579, 599, 662, 689, 796, 840, 960, 994, 1015, 1024, 1125, 3813, 3818, 3825, 3856, 3869
	S	130, 157, 191, 222, 368, 373, 396, 407, 420, 469, 508, 517, 522, 676, 688, 803, 805, 906, 926, 953, 960, 1022, 3806, 3817, 3834, 3848, 3848

Note that the inclusion of ZPE and statistical mechanics contributions (G_{298})—responsible for 4 to 7 kcal/mol each, depending on species—is important for quantitative results.

3.2.3. Pentacoordinate vs. tetracoordinate silicate anion

Finally we address the issue of the 5-coordinate vs. 4-coordinate silicate anion by calculating the aqueous thermochemistry of the reaction $\text{H}_3\text{SiO}_4^- + \text{H}_2\text{O} = \text{H}_5\text{SiO}_5^-$. We use a standard thermodynamic cycle consisting of the following steps:

- (1) reverse hydration of reactants to the gas-phase standard state (the ideal gas at temperature 298.15 K and pressure 0.1 MPa; see Section 2.1),
- (2) the gas-phase reaction at the same standard-state conditions, and

Table 7. Aqueous-phase results with new atomic radii.

Species	SCFE (hartree)	ΔG_h^* (kcal/mol)
H ₄ SiO ₄	-593.0517	-21.0
H ₃ SiO ₄ ⁻	-592.5881	-86.8
H ₂ SiO ₄ ²⁻	-592.1118	—
HSiO ₄ ³⁻	-591.6293	—
SiO ₄ ⁴⁻	-591.1360	—
H ₅ SiO ₅ ⁻ (A)	-669.0384	-85.5
H ₅ SiO ₅ ⁻ (B)	-669.0385	-78.8
H ₂ O	-76.4505	-10.4
H ₃ O ⁺	-76.8717	-102.8
OH ⁻	-75.9687	-103.8
H ⁺	—	-267.1 ^a

^a Using $\Delta G_h^*(\text{H}^+ + \text{OH}^-) = -370.9$ kcal/mol (Table 1b).

- (3) hydration of the product (considering the more stable conformation B).

If solvation effects are neglected, we consider only the gas-phase reaction energetics (step 2) with corresponding calculated thermochemical quantities in Table 3. The gas-phase SCF energy difference is then $\Delta\text{SCFE} = -668.9129 + 592.4498 + 76.4339 = -0.0292$ hartree = -18.3 kcal/mol. After including the zero point energy difference $\Delta\text{ZPE} = 46.0 - 28.7 - 13.4 = +3.9$ kcal/mol, we get $\Delta E = \Delta\text{SCFE} + \Delta\text{ZPE} = -14.4$ kcal/mol. Finally, after adding the statistical mechanics contributions for 298 K, $\Delta G_{298} = -19.8 + 18.4 + 11.1 = +9.7$ kcal/mol, we get the standard Gibbs free energy of the reaction $\text{H}_3\text{SiO}_4^- + \text{H}_2\text{O} = \text{H}_5\text{SiO}_5^-$ in the gas phase $\Delta G^{\circ}(\text{gas}) = \Delta\text{SCFE} + \Delta\text{ZPE} + \Delta G_{298} = -4.7$ kcal/mol. Thus this reaction is thermodynamically favorable in the gas phase by ~5 kcal/mol, when the ZPE and statistical mechanics contributions are properly taken into account.

However, we get a different picture when solvation effects are considered. For step 1, we use the experimental value for the Gibbs free energy of hydration of water $\Delta G_h^{\circ}(\text{H}_2\text{O}) = -2.05$ kcal/mol (see the second column of Table 1b corresponding to our choice of the gas-phase standard state). For H_3SiO_4^- we use the calculated Gibbs free energy of hydration $\Delta G_h^*(\text{H}_3\text{SiO}_4^-)$ from Table 7, converted to the chosen standard state $\Delta G_h^{\circ}(\text{H}_3\text{SiO}_4^-) = \Delta G_h^*(\text{H}_3\text{SiO}_4^-) + 1.9$ kcal/mol = -86.8 + 1.9 = -84.9 kcal/mol. Similarly for step 3, we take the calculated Gibbs free energy of hydration $\Delta G_h^*(\text{H}_5\text{SiO}_5^-)$ from Table 7, converted to the chosen standard state $\Delta G_h^{\circ}(\text{H}_5\text{SiO}_5^-) = \Delta G_h^*(\text{H}_5\text{SiO}_5^-) + 1.9$ kcal/mol = -78.8 + 1.9 = -76.9 kcal/mol. Now we can calculate the

Table 8. Thermochemistry of silicic acid deprotonation $H_{5-i}SiO_4^{-i+1} = H^+ + H_{4-i}SiO_4^{-i}$ in aqueous solution with new atomic radii.

i	1	2	3	4
$\Delta SCFE$ (kcal/mol)	25.7	33.7	37.6	44.4
ΔZPE (kcal/mol)	-7.0	-6.5	-6.9	-6.8
ΔG_{298} (kcal/mol)	-6.4	-5.6	-5.9	-4.4
ΔG° (kcal/mol)	12.3	21.6	24.8	33.2
ΔG° (exp) (kcal/mol)	13.4	18.3	23.2 ^a	28.1 ^a

For experimental values cf. Sefcik and McCormick, 1997b.

^a Values for $i = 3, 4$ estimated by linear extrapolation from $i = 1, 2$.

standard Gibbs free energy of the reaction $H_3SiO_4^- + H_2O = H_5SiO_5^-$ in the aqueous phase as the sum of contributions from steps 1, 2, and 3: $\Delta G^\circ(\text{aqueous}) = +2.05 + 84.9 - 4.7 - 76.9 = +5.4$ kcal/mol. We note that using the default atomic radii we get $\Delta G = +6.8$ kcal/mol. This indicates that details about parameters in the solvation model are not important to achieve the conclusion: inclusion of hydration in thermodynamic calculations is necessary to be consistent with the experimentally observed lack of pentacoordinate silicic acid anions in aqueous solutions.

4. CONCLUSIONS

We compared gas-phase and solvated DFT calculations of monomeric anions of silicic acid to assess solvent effects on the thermochemistry of silicic acid deprotonation. We showed that appropriate inclusion of solvation in quantum chemical calculations is critical for correct prediction of coordination and thermochemistry of silicate anions in aqueous solutions. Multiply charged anions of silicic acid were found to be electronically unstable in the gas phase; thus, it is not useful to use thermodynamic cycles involving these species in thermodynamic calculations. However, polarizable continuum effect is sufficient to stabilize these highly charged anions and solvated calculations were used to directly compute their thermodynamic quantities. When we included the ZPE and statistical mechanics contributions to free energy, we obtained accurate Gibbs free energies for successive deprotonations of silicic acid in aqueous solutions. While the five-coordinated silicate anion was found to be more stable in the gas phase than the four-coordinated one (by 18 and 5 kcal/mol in the SCF energy and Gibbs free energy, respectively), it was less stable by 5 kcal/mol in the Gibbs free energy when hydration effects were appropriately accounted for. We demonstrated that solvated DFT calculations present a valuable methodology enabling one to go beyond gas-phase modeling to make more accurate predictions of geochemical processes involving silicate anions in aqueous solutions and at mineral interfaces.

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