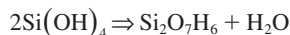


Theoretical study on the dimerization of $\text{Si}(\text{OH})_4$ in aqueous solution and its dependence on temperature and dielectric constant

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Abstract—Energetics for the condensation dimerization reaction of monosilicic acid:

have been calculated quantum mechanically, in gas-phase and aqueous solution, over a range of temperatures and dielectric constants. The calculated gas phase energy, E_g , for this reaction is -6.6 kcal/mol at the very accurate composite G2 level, but the vibrational, rotational and translational contributions to the free energy in the gas-phase, ΔG_{VRT} , sum to $+2.5$ kcal/mol and the hydration free energy contribution calculated with a polarizable continuum model, $\Delta\Delta G_{\text{COSMO}}$, for a dielectric constant of 78.5, is about $+6.2$ kcal/mol. Thus, the free energy change for the reaction in aqueous solution at ambient conditions is about $+2.1$ kcal/mol and the equilibrium constant is $\sim 10^{-1.5}$, in reasonable agreement with experiment. As T increases, ΔG_{VRT} increases slowly. As the dielectric constant decreases (for example, under high T and P conditions in the supercritical region), $\Delta\Delta G_{\text{COSMO}}$ decreases substantially. Thus, at elevated T and P , if the effective dielectric constant of the aqueous fluid is 10 or less, the reaction becomes much more favorable, consistent with recent experimental observations. The $P\Delta V$ contribution to the enthalpy is also considered, but cannot be accurately determined.

We have also calculated ^{29}Si -NMR shieldings and Raman frequencies for $\text{Si}(\text{OH})_4$, $\text{Si}_2\text{O}_7\text{H}_6$ and some other oligomeric silicates. We correctly reproduce the separation of monomer and dimer peaks observed in the ^{29}Si -NMR spectra at ambient T and P . The Raman spectral data are somewhat ambiguous, and the new peaks seen at high T and P could arise either from the dimer or from a 3-ring trimer, which is calculated to be highly stabilized entropically at high T . Copyright © 2005 Elsevier Ltd

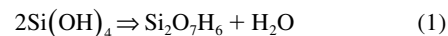
1. INTRODUCTION

It has long been known that the solubilities of the SiO_2 polymorphs in water increase with increasing T (Walther and Helgeson, 1977, and references therein). There has also been considerable speculation about the existence of oligomeric Si species in aqueous solutions. The possible importance of silicate oligomers in a number of geochemical processes has been discussed by Crerar et al. (1981). Early studies using ^{29}Si -NMR (Cary et al., 1982) at room T and P showed a small peak consistent with the presence of a small amount of oligomer, in addition to the monomer $\text{Si}(\text{OH})_4$. This additional peak, with a shift ~ 9.3 ppm more negative than that for $\text{Si}(\text{OH})_4$, was assigned to the dimer $\text{Si}_2\text{O}_7\text{H}_6$ on the basis of systematic trends in NMR shift observed for anionic species in alkaline silicate solutions (Harris et al., 1981). Similar ^{29}Si -NMR results were obtained by Meinhold et al. (1985) for supersaturated silica solutions at room T and P .

Recently Zotov and Keppler (2000, 2002) have presented Raman spectral evidence for the presence of much larger concentrations of the dimeric species in aqueous solution under supercritical conditions (T above 1120–1170 K and P above 12–13 kbar). Newton and Manning (2002, 2003) have presented solubility studies supporting the new dimer model of Zotov and Keppler. Their analysis indicated that at 1070 K and 12 kbar pressure $\sim 70\%$ of the silica in solution consisted of

dimers. Zhang and Frantz (2000) had earlier arrived at similar conclusions regarding the stability of the dimer. Roughly 20 yr elapsed between the experiments of Cary et al. (1982) and Zotov and Keppler (2000) because working under supercritical conditions is very difficult. In addition, the experiment performed under these conditions by Zotov and Keppler was Raman spectroscopy, which is a powerful technique but not so easily interpretable as NMR. To substantiate the identification of such dimeric species by matching their experimental NMR and Raman spectra and to analyze the different components of the reaction free energy and their changes with temperature and pressure, quantum mechanical computations can be very powerful.

The first step in the condensation polymerization process for monosilicic acid:



is obviously of interest in aqueous geochemistry since it may influence the overall solubility of SiO_2 in aqueous solutions and may control the energetics and kinetics of silica precipitation. It is also of interest in materials science because of its importance in sol-gel synthesis of zeolites and other silicates and aluminosilicates. A number of theoretical studies in the chemistry and materials science literature have considered this reaction either in passing (Johnson et al., 1989; Field and Olson, 2001; Ignatov et al., 2003; van Duin et al., 2003) or in considerable detail (Kudo and Gordon, 1998; Cypryk and Apeloig, 2002; Catlow et al., 2003). In the studies of Kudo and Gordon (1998) and

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Table 1. Calculated energy change (in kcal/mol) for the gas-phase reaction $2 \text{Si}(\text{OH})_4 \rightleftharpoons \text{Si}_2\text{O}_7\text{H}_6 + \text{H}_2\text{O}$ calculated at various quantum mechanical levels.

Method	ΔE_g
pol. SBK HF	-3.2
pol. SBK MP2	-2.8
6-311+G(2d,p) BLYP	-0.6
6-311+G(2d,p) B3LYP	-1.1
6-31G* HF	-10.0
6-31G* MP2	-11.0
6-311+G(2d,p) HF	-2.5
6-311+G(2d,p) MP2	-2.8
QCISD(T)/6-31G(d)//MP2/6-31G*	-3.3
QCISD/6-311G(d,p)//MP2/6-31G*	-4.0
G2MP2	-6.6
G2	-6.6

Cypryk and Apeloig (2002) the focus has been not on the energetics of the reactants and products but on the activation energy for the reaction and in some cases its dependence upon the participation of water. However, hydration effects on the energetics (beyond the effects of a few explicit water molecules) have not been considered. There have been some attempts (e.g., Kudo and Gordon, 1998) to establish the dependence of the energy calculated for the gas-phase condensation reaction upon the computational method used.

DeJong and Brown (1980) long ago addressed the question of polymerization in silicate and aluminosilicate solutions using semiempirical MO methods. Rustad and Hay (1995) and Felmy et al. (2001) have investigated silica speciation, primarily in alkaline environments, using force fields sometimes partly parameterized from quantum mechanical calculations and sometimes partly fitted to species distributions evaluated from NMR. Tossell and Sahai (2000) studied the acid dissociation of the silanol group in a number of oligomeric silicate models using a quantum chemical approach, establishing that the silanol group generally becomes more acidic with increasing oligomerization. The $\text{Si}_2\text{O}_7\text{H}_6$ molecule has been treated by a number of researchers, but the focus has usually been on its structure and reactivity (e.g., Lasaga and Gibbs, 1987; Xiao and Lasaga, 1996), with no information given on its other properties. ^{29}Si -NMR shieldings have been reported for $\text{Si}_2\text{O}_7\text{H}_6$ by Moravetski et al. (1996), which were in at least semiquantitative agreement with experiment.

In our recent studies of reactions in aqueous solution (e.g., Tossell, 2003) standard methods have been used to evaluate vibrational, rotational and translational contributions to the free energy at 298 K and polarizable continuum methods have been used to evaluate hydration contributions to the free energy for ambient water, with a dielectric constant of 78.5. To our knowledge, no one has attempted to apply a quantum mechanical approach to the evaluation of reaction energies for silicates in water above its critical point of 647 K and 0.22 kbar. We here attempt to evaluate the energetics of silicic acid oligomerization for supercritical conditions as high as 1200 K and 10 kbar, matching those used in the experiments of Zotov and Keppler (2000, 2002). The most serious problems in extending our studies to high T and P comes from the increase in importance

of some energetic terms which were small at low T and P and so could be either ignored or evaluated with lesser accuracy.

2. COMPUTATIONAL METHODS

We use the methods of molecular quantum mechanics, specifically the Hartree-Fock (HF) method, the Moller-Plesset many body perturbation theory method to second order (MP2; Head-Gordon et al., 1988), the quadratic configuration interaction method with single and double substitutions (QCISD; Pople et al., 1987) and the very accurate composite methods G2 and G2MP2 (Curtiss et al., 1993) which accurately determine the effects of both basis set extension and electron correlation. All these methods are described in standard computational chemistry monographs, such as Jensen (1999). The MP2, QCISD, G2 and G2MP2 methods incorporate dynamic correlation in the motion of electrons, which is neglected at the HF level. They typically provide much more accurate bond energies and somewhat better equilibrium geometries than does the HF method. However, they are more demanding of computer time than HF, particularly the G2 and G2MP2 methods. We have employed the MP2 approach as our base method because of its accuracy and efficiency. We have also tested several forms of density functional theory, DFT, particularly the BLYP potential (Becke, 1993; Lee et al., 1988) as well as HF-DFT hybrids like B3LYP.

The basis sets used to expand the molecular orbitals were generally those of all electron type, such as 6-31G* and 6-311+G(2d,p) (Hehre et al., 1986) but in some preliminary calculations we have used valence-electron only, relativistic effective core potential type bases (Stevens et al., 1992), which we designate SBK.

For all the species considered we have determined equilibrium geometries in the gas-phase and have evaluated vibrational frequencies, zero-point vibrational energies (ZPE) and vibrational, rotational and translational (VRT) contributions to the gas-phase free energy. The necessary equations for the ZPE and VRT contributions are given in Hehre et al. (1986) and incorporated into the GAMESS and GAUSSIAN codes. The vibrational contributions have been scaled using the normal factors (Pople et al., 1993, for HF; Wong, 1996, for DFT).

To approximate hydration energies we have used the COSMO (Conductor-like Screening MO method; Klamt and Schüürmann, 1993; Truong and Stefanovich, 1995) version of the self-consistent reaction field polarizable continuum method. This is a very rapid and efficient technique which utilizes a nonspherical cavity about the solute and gives results very similar to those from older nonspherical cavity polarizable continuum models, but at much less computational cost. Nonetheless it still suffers from the main ambiguity of polarizable continuum models: the lack of uniqueness in the choice of the solute cavity. The implementation of this method in GAUSSIAN98 (Frisch et al., 1998) also includes several small energetic terms which are evaluated semiempirically, such as the cavitation energy and the dispersion energy. It is important to realize that any polarizable continuum model of hydration is basically a simulation of the real system and involves very serious approximations and that the hydration energy differences evaluated for reactions, particularly those involving ions, are invariably much less accurate than are the corresponding

Table 2. Calculated values of ΔG_{VRT} (kcal/mol) for the reaction $2 \text{Si(OH)}_4 \Rightarrow \text{Si}_2\text{O}_7\text{H}_6 + \text{H}_2\text{O}$ at various temperature (6-31G* HF calculations, with vibrational correction factors of 0.893).

T (K)	0	298	500	700	900	1100
ΔG_{VRT}	2.1	2.5	3.0	3.2	3.3	3.4

gas-phase energies. However, we can anticipate that these hydration energy differences will have small absolute errors for reactions of neutral molecules and for isocoulombic reactions (in which the magnitudes of the squared ion charges for reactants and products are the same). To evaluate the hydration energy for any value of T and P other than ambient we simply adjust the value of the dielectric constant. This approach may not accurately treat small changes in the cavitation energy or the dispersion energy (both of which are small to begin with) but the dominant electrostatic term will be calculated correctly.

For some species we calculated equilibrium geometries within a polarizable continuum representation of the solvent, using COSMO. However, the change in bond distances in the COSMO optimizations was always less than 0.01 Å and the change in total energy no more than 1 kcal/mol. Therefore, we decided to use only the gas-phase equilibrium geometries in the COSMO calculations, without reoptimizing the geometries. This does not necessarily mean that the effect of solvent is really that small, since COSMO may well underestimate the effect of the solvent water on the structure.

We use the quantum chemical software GAMESS (Schmidt et al., 1993) and GAUSSIAN98 (Frisch et al., 1998) for the calculations. It is worth noting that reaction energies in aqueous solution can be obtained from ab initio molecular dynamics (Car and Parrinello, 1985), although the computational demands of this approach are still enormously high. This method has recently been applied to the oligomerization of carbohydrates through formation of glycosidic bonds (Stubbs and Marx, 2003).

3. RESULTS AND DISCUSSION

3.1. Energetics

Calculations of the gas-phase energies of the condensation dimerization reaction are given in Table 1 at a number of different quantum mechanical levels. It is clear that the energy change for this reaction is fairly small in magnitude (0–10 kcal/mol) and that the percent changes with method and basis set are rather large. Although there does not seem to be any directly determined experimental value for the energy of this reaction, a naive use of the data from the NBS tables (Wagman et al., 1982) gives a free energy change of + 0.7 kcal/mol, using the entries for unspecified “cr” (crystalline?) versions of Si(OH)₄ and Si₂O₇H₆. In Table 1 we order the methods we have employed from top to bottom in approximate order of their anticipated accuracy, with the QCISD and the even more accurate composite G2MP2 and G2 methods at the bottom expected to be the most accurate. The G2MP2 and G2 results are in very close agreement and the large basis set QCISD and MP2 results are fairly close to the G2 results. It appears that calculations at high quantum mechanical levels are required to give results converged with respect to both method and basis.

Curtiss et al. (1993) determined that average errors in energetic quantities (such as heats of formation) for an extensive test set of gas-phase molecules were ~ 1.2 kcal/mol at the G2 level. The error in our G2 calculated dimerization energy is probably of the same size or even smaller, since the reaction involves mainly a rearrangement, rather than a breaking, of bonds. Several DFT methods in addition to BLYP were also tried but always gave rather small magnitudes for the energy change, as has been observed for related siloxane reactions by Cypryk and Apeloig (2002) and Ignatov et al. (2003). By contrast, the DFT calculations of van Duin et al. (2003) gave -15.0 kcal/mol for the energy change in the dimerization reaction. This indicates that DFT methods must be used with considerable caution if highly accurate energetics are required for such reactions.

To obtain reaction free energies in solution we must add to these gas-phase energies the vibrational, rotational and translational contributions to the free energy ΔG_{VRT} and the hydration contribution to the free energy, which we designate $\Delta \Delta G_{\text{COSMO}}$ (where $\Delta \Delta G_{\text{COSMO}}$ is the sum of the COSMO hydration energies of the products minus that for the reactants). We evaluate ΔG_{VRT} at the 6-31G* HF level and 298 K and 1 atm pressure, with the usual scaling factor of 0.893 for the vibrational frequencies (Pople et al., 1993) and we evaluate the hydration free energy $\Delta \Delta G_{\text{COSMO}}$ using 6-31G* HF geometries, the 6-31G* basis set and the COSMO method with a dielectric constant $D = 78.5$. These approaches give values of + 2.5 and + 6.2 kcal/mol, respectively, for the VRT gas-phase contribution to the reaction free energy and for the hydration contribution. Our final free energy change in aqueous solution is then given as:

$$\Delta G_{\text{aq}} = \Delta E_{\text{g}} + \Delta G_{\text{VRT}} + \Delta \Delta G_{\text{COSMO}} \quad (2)$$

and its calculated value at ambient conditions is + 2.1 kcal/mol (using the G2 value of -6.6 kcal/mol for ΔE_{g}). This value of ΔG_{aq} would correspond to an equilibrium constant for the condensation dimerization reaction 1 of $\sim 10^{-1.5}$ at $T = 298$ K. This is consistent with the very small intensity (on the order of a few percent of the main monomer signal) for the ²⁹Si-NMR peak attributed to the dimer under ambient conditions (Cary et al., 1982; Meinhold et al., 1985).

Now we need to assess the changes in ΔG_{VRT} and $\Delta \Delta G_{\text{COSMO}}$ for other temperatures and dielectric constants. In Table 2 we show calculated changes in ΔG_{VRT} at a series of temperatures from 0 to 1100 K (obtained by simply changing the temperature in the ΔG_{VRT} calculation in GAMESS) and in Table 3 we show changes in $\Delta \Delta G_{\text{COSMO}}$ for a series of dielectric constants from 78.5 to 1.9. Plots of ΔG_{VRT} vs. T and $\Delta \Delta G_{\text{COSMO}}$ vs. the quantity $(1 - 1/D)$ are shown in Figures 1 and 2, respectively. ΔG_{VRT} vs. T has been fitted to a second-order polynomial but the trend is not far from being linear. For the condensation dimerization reaction the zero-point energy calculated at the 6-31G* HF level is quite small, less than 0.1

Table 3. Calculated values of $\Delta \Delta G_{\text{COSMO}}$ (kcal/mol) for the reaction $2 \text{Si(OH)}_4 \Rightarrow \text{Si}_2\text{O}_7\text{H}_6 + \text{H}_2\text{O}$ for various dielectric constants (from 6-31G* HF COSMO calculations).

D	78.5	38.2	20.7	10.4	3.3	1.9
$\Delta \Delta G_{\text{COSMO}}$	6.2	6.1	5.8	5.6	4.1	2.7

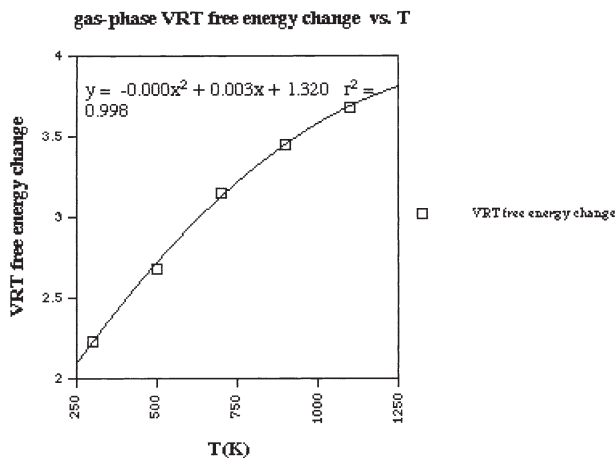


Fig. 1. Calculated gas-phase VRT contribution to the reaction free energy change vs. T (fitted to second-order polynomial for range 200–1100 K).

kcal/mol. More detailed inspection of the calculated energies indicates that the VRT contribution to the gas-phase free energy is determined almost entirely by the temperature dependent part of the vibrational enthalpy. The vibrational enthalpy term has large contributions from low frequency vibrations which are strongly excited at moderate temperatures and $\text{Si}_2\text{O}_7\text{H}_6$ has a number of such low energy vibrational modes, while such modes are absent in the monomer and in water.

While our ΔG_{VRT} results are certainly valid for the gas-phase, one might question whether it is appropriate to extend them to aqueous solution since the low energy modes of the dimer may be strongly modified or suppressed in solution. The nature of the rotational and translational motions of simple solutes like CH_4 in simple solvents like $\text{Ar}(\text{l})$ have been studied for some time (Ewing, 1969), but no such spectral information is available for $\text{Si}(\text{OH})_4$ or $\text{Si}_2\text{O}_7\text{H}_6$ in aqueous solution. In general, the translational and rotational motions are expected to be suppressed, although they may be converted to low-frequency vibrational motions, e.g., hindered rotations, which may make similar contributions to the thermodynamic functions. The molecular vibrations persist, although they can certainly be perturbed and mixed with solvent modes. The possible energetic effects of such changes in VRT contributions have even been used to explain the mechanism of enzyme catalysis (e.g., Page and Jencks, 1971). Fortunately, our ΔG_{VRT} calculations indicate that the rotational and translation contributions to the free energy change for the condensation dimerization reaction are very small (≤ 0.1 kcal/mol) and that the vibrational contribution is dominant. Thus, if the low energy vibrational modes are not too strongly perturbed in aqueous solution our analysis should remain valid. Recently, Leung et al. (2004) have examined the source of the entropy reduction which occurs when a gas-phase molecule is moved into solution and have concluded that the main contribution to the entropy change comes from cavity formation in the solvent, a term which is incorporated (at least approximately) in the normal implementation of COSMO.

$\Delta \Delta G_{\text{COSMO}}$ scales linearly with the quantity $(1 - 1/D)$, as expected from the classic Onsager model for the hydration of

ions and polar molecules. However, the decrease in $\Delta \Delta G_{\text{COSMO}}$ with increase in D is fairly slow until D itself becomes quite small (remember D is ~ 78.5 for ambient water). The basic reason for the positive value of the hydration contribution to the reaction free energy is the small magnitude of the hydration energy for the dimer. The COSMO calculations indicate that the hydration energy arises almost entirely from the electrostatic part of $\Delta \Delta G_{\text{COSMO}}$. We speculate that in the dimerization reaction one of the electronegative O atoms is essentially moved from the “exterior” of the monomer to the “interior” of the dimer, where it interacts less strongly with the solvent. A more detailed analysis of the COSMO energetics (which may not be justified due to the parametric nature of the COSMO method) would be needed to substantiate this point. Equivalently, we could speculate that bridging O atoms (BO) interact less favorably with water than do nonbridging O atoms (NBO) or O-H groups. If this interpretation is correct, a positive value for the hydration contribution to the reaction free energy change will be a general property of such polymerization reactions. Indeed, we will see from the data in Table 4 that that is the case (see below). Severance and Jorgensen (1994) have seen effects on reaction energies of the same sign and similar magnitude for cases in which aldehydes are rearranged to ethers (the Claisen rearrangement).

Of course the bulk dielectric constant of water at high T and P will be considerably smaller than its value of 78.5 under ambient conditions (Pitzer, 1983). Based on the MD simulations of Wasserman et al. (1994) we would expect that at the highest P and T conditions considered by Zotov and Keppler ($T = 1173$ K, $P = 9.2$ kbar) the dielectric constant would be around 10. For example, Wasserman et al. (1994) calculate $D = 13.3$ at $T = 1040$ K and $P = 15.1$ kbar. What is not so clear is whether such bulk values are appropriate for describing the energetics of hydration in a compressible solvent like supercritical water. It is clear from many studies (e.g., Liu et al., 2003) that ions in supercritical aqueous solutions essentially create local environments with higher effective dielectric constants than the bulk value for those T, P conditions. However the simulations of Luo and Tucker (1996) on anisole hydrolysis in supercritical water suggest that such effects are much smaller for neutral molecules than for ions.

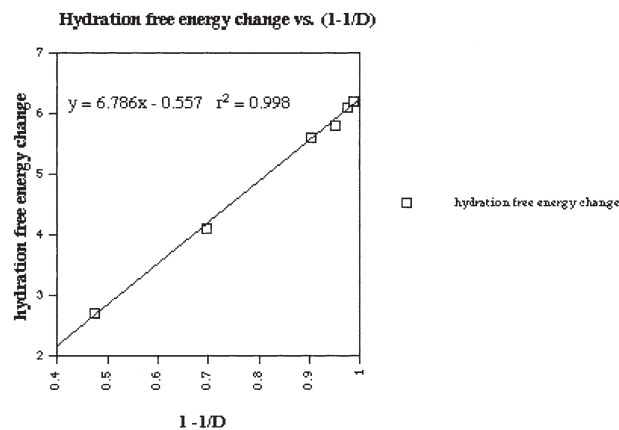


Fig. 2. Hydration free energy change vs. $(1 - 1/D)$, where D is the dielectric constant.

Table 4. Calculated gas-phase energies, ΔE_g , for formation of various dimers and the cyclic trimer from monomeric units (evaluated at the 6-311+G(2d,p) MP2 level), VRT contributions to the gas-phase free energy ΔG_{VRT} (evaluated at the 6-31G* HF level) and hydration energies, $\Delta\Delta G_{COSMO}$, for $D = 78.5$ (all in kcal/mol).

Dimer	Type	ΔE_g	ΔG_{VRT}	$\Delta\Delta G_{COSMO}$	ΔG_{aq}
Si ₂ O ₇ H ₆	Si-O-Si	-3.9	+0.5	+19.4	+16.0
Si ₂ O(CH ₃) ₆	Si-O-Si	-6.0	+1.8	+4.6	+0.4
Si ₂ O ₇ H ₆	Si-O-Si	-2.8	+2.5	+6.2	+5.9
Si ₂ O ₇ H ₅	Si-O-Si	-22.6	+2.1	+21.1	+0.6
Si ₃ O ₉ H ₆	3Si-O-Si	+4.4	-8.2	+4.8	+0.8
SiAlO ₇ H ₆ ⁻¹	Si-O-Al	-28.1	+4.3	+26.0	+2.2
SiBO ₆ H ₅	Si-O-B	+7.0	+0.9	+6.8	+14.7
AlBO ₆ H ₅ ⁻¹	Al-O-B	-8.4	+0.3	+7.2	-0.9

One term we have not yet considered is the $P\Delta V$ contribution to the enthalpy. In all our previous studies (e.g., Tossell, 2003) we evaluated energetics near ambient pressure, rather than under supercritical conditions. This term can be expressed in units of kcal/mol as:

$$P\Delta V = 0.0241 \times P(\text{kbar}) \times \Delta V(\text{cm}^3/\text{mol}) \quad (3)$$

This term is negligible at $P = 1$ atm for any normal change in reaction volume involving only condensed phase materials (with small molar volumes) but can become substantial when the p -values are in the kbar range. To evaluate this term we need to determine ΔV for the reaction. There is in principle no unambiguous way to do this quantum mechanically for isolated individual molecules, although naive application of the electron density contour approach implemented in GAUSSIAN (for slightly different purposes) produces 14.2 cm³/mol for the volume of the water molecule, while a recent estimate of the volume of liquid water (Richet et al., 2000) is 12.0 cm³/mol, in the same range as the calculation. Using the same GAUSSIAN procedure to determine the molar volumes of the Si(OH)₄ and Si₂O₇H₆ molecules involved in the dimerization reaction gives a volume change of -5.0 cm³/mol (if we use the 6-311+G(2d,p) MP2 geometries for Si(OH)₄ and Si₂O₇H₆, the highest level method and basis we have used for geometry optimization, which gives a $\angle\text{Si-O-Si} = 148^\circ$ in the dimer). At a pressure of 15 kbar this gives a change in reaction enthalpy of -1.8 kcal/mol. Thus, this effect is certainly not negligible but neither is it overwhelmingly large, even at very high P . Since we cannot evaluate it accurately, we choose to ignore it at this time.

These results indicate that the condensation dimerization of Si(OH)₄ which is slightly favorable in the gas-phase becomes unfavorable in aqueous solution at ambient conditions. However, at high T and P (with a low effective dielectric constant) the reaction can become much more favorable. This would

certainly be qualitatively consistent with the spectral data of Zotov and Keppler (2000, 2002), indicating increased stability for Si₂O₇H₆, and with the solubility analyses of Newton and Manning (2002, 2003). Determining the exact balance of temperature and dielectric constants effects is, however, difficult. Based on the results in Table 2 an increase in T from 298 to 1100 K would make the reaction ~ 1.3 kcal/mol less favorable due to the increase in ΔG_{VRT} . For the reduction in the hydration free energy term $\Delta\Delta G_{COSMO}$ in Table 3 to compensate for this increase, the dielectric constant would have to be around 4 or lower. Without further details on the properties of the supercritical solvent under such conditions it is hard to determine an exact change in the free energy.

We have also examined the energetics of such condensation polymerization processes for a number of other pairs of monomers, with the results shown in Table 4. In each case we have employed the 6-311+G(2d,p) MP2 level of theory to evaluate the gas-phase energy, since that gave reasonable results (-2.8 kcal/mol compared to -6.6 kcal/mol for the best calculation) for Si₂O₇H₆, with reasonable computational effort. For all these condensation polymerization reactions the $\Delta\Delta G_{COSMO}$ hydration free energy term is positive, indicating that the reaction is disfavored by hydration effects. The ΔG_{VRT} term is also positive for all the reactions in which the number of molecules is conserved (every one in Table 4 expect the formation of the 3-ring cyclic trimer), indicating that the reactions are disfavored by increasing temperature in the gas phase. The first five entries in Table 4 involve the formation of Si-O-Si bonds, the first four with varying terminal ligands, while the fifth corresponds to formation of the closed "3-ring," i.e., with three Si atoms within the ring. The most favorable reaction free energy is found for the case of -CH₃ terminal ligands, with a free energy change very close to zero even in aqueous solution. In practice, such a dimerization reaction of methylsiloxanes would be performed in organic solvents with lower dielectric con-

Table 5. Calculated NMR shieldings (in ppm) for various species and basis sets, using the Hartree-Fock GIAO method.

Basis, method/molecule	6-31G* free HF (MP2)	6-31G* ... n H ₂ O	6-311+G(2d,p) free	6-311+G(2d,p) ... n H ₂ O
Si(OH) ₄	510.2 (487.2)	511.1	455.8	457.4
Si ₂ O ₇ H ₆	519.9 (503.8)	519.0(av)	468.8	467.4
Si(OH) ₃ O ⁻¹	506.7	512.8	451.1	457.2
Si ₂ O ₇ H ₅ ⁻¹	510.4	517.8	455.9	465.2
Si ₃ O ₉ H ₆	525.5	—	474.0	—

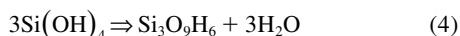
Table 6. Calculated symmetric stretching frequencies for Si(OH)₄, free, hydrated, in a polarizable continuum representation of water, and with anharmonic corrections.^a

Model and method	Calculated ν (cm ⁻¹)	Scaled ν (cm ⁻¹), using standard factors ^b
Si(OH) ₄ 6-31G* HF	816	729
Si(OH) ₄ 6-31G* HF anharmonic	810	723
Si(OH) ₄ 6-31G** HF	820	732
Si(OH) ₄ 6-31G* MP2	765	719
Si(OH) ₄ 6-31G* MP2 anharmonic	756	713
Si(OH) ₄ 6-31G** MP2	764	721
Si(OH) ₄ 6-311+G(2d,p) MP2	768	724
Si(OH) ₄ 6-311+G(2d,p) B3LYP	759	729
Si(OH) ₄ 6-31G* HF COSMO	805	719
Si(OH) ₄ . . . 4 H ₂ O 6-31G* HF	809	722
Exp.		≈770

^a Clabo et al. (1988).¹

^b Pople et al. (1993).¹

stants, so the solvation contribution would be smaller (less positive) and the overall free energy would be negative. This is consistent with the ready polymerization of methyl siloxanes in organic solvents. The fourth reaction involves a neutral monosilicic acid species condensing with the corresponding anion to give a monoanion product. For this species the reaction free energy in aqueous solution is less positive than for the neutral analog, although we must be cautious in this interpretation because it involves the balance between a much more favorable gas-phase energy and a much less favorable hydration energy, due to the loss of the large hydration energy of the monomeric anion. Certainly, all the experimental evidence suggests that dimers and other higher oligomers are much more prominent in alkaline silicate solutions containing silicate anions (Harris et al., 1981; Sjoberg, 1996) than in silica solutions with pH's in the neutral or acidic range. For the fifth entry we find that the 3-ring species is unfavorable from the point of view of gas-phase energetics and has a sizable positive value for its hydration free energy contribution. However, in its formation reaction:



the number of molecules increases, which gives a significant $-\Delta S$ term, strongly driving the reaction. This term becomes even more negative at high T (see below) and provides a strong driving force for the formation of such ring species. The sixth case in Table 4 corresponds to formation of a Si-O-Al linkage, which has been seen in Raman spectroscopy in both alkaline and acidic solutions (Gout et al., 2002). Our calculations indicate about the same stability for this species as for the silicate dimer anion. The seventh case involves creation of a dimer with a Si-O-B bond (with the B three-coordinate), which is found to be strongly unfavorable, while in the eighth case the formation of a Al-O-B (three-coordinate B) bond is found to be considerably more favorable, in accord with the observations of such species by Fouquet et al. (2002). For each of these cases a more extensive analysis of T, P and dielectric constant effects on the energetics would be worthwhile.

3.2. Spectra

We have also calculated NMR and Raman spectra for the various silicate species to determine what methods, basis sets and models are needed to accurately match the experimental data. NMR shifts for the various species obtained using different approaches are reported in Table 5. The experimental shift of the dimer vs. the monomer is observed to be -9.3 ppm in neutral solution (Cary et al., 1982) and about -8.6 ppm in alkaline solution (Harris et al., 1981). The calculated ²⁹NMR shieldings for each of the species increases by 1–2 ppm as explicit waters are added (4 H₂O molecules for the monomer and 7 H₂O molecules for the dimer). Such small increases have been seen in similar calculations on static molecules (Moravetski et al., 1996) as well as for structures obtained from molecule dynamics simulations (Krishnamurty et al., 2003). Our best calculations, HF 6-311+G(2d,p) on the explicitly hydrated species, give a shielding of the dimer vs. the monomer of 10.0 ppm (467.4–457.4 ppm) for the neutral species and 8.0 ppm (465.2–457.2 ppm) for the anions. The 3-ring (or “cyclic trimer”) species Si₃O₉H₆ is ~ 18 ppm more shielded than the monomer (comparing the bare molecules only, without hydration). These results are in general agreement with those of Moravetski et al. (1996), who obtained a shielding of 6.0 to 12.3 ppm for the dimer vs. the monomer, depending upon details of the geometry, using similar theoretical methods applied to the bare molecules.

Thus we can confirm that the species seen by Cary et al. (1982) and Meinhold et al. (1985) was indeed Si₂O₇H₆. Note that if the 3-ring species Si₃O₉H₆ were to occur for silica solutions under other T, P conditions it could easily be recognized by its larger NMR shift compared to the monomer.

Results of calculations of the Raman spectra of Si(OH)₄, Si₂O₇H₆ and related molecules are given in Tables 6–9. Calculated Raman spectra have been previously given for SiF₄ and Si(OH)₄ by Hess et al. (1986, 1987). For Si(OH)₄ the standard methods, such as 6-311+G(2d,p) MP2, used with standard scaling factors, give only mediocre agreement with experiment, consistently giving scaled frequency values low by 40 or more cm⁻¹ for the symmetric stretching vibration. Nor does the incorporation of anharmonicity (a very demanding calculation, see Clabo et al., 1988) give much change (765 harmonic vs. 756 cm⁻¹ anharmonic at the 6-31G* MP2 level in our calculations). Use of the hybrid HF-DFT approach, specifically the B3LYP functional, with standard scaling factors from Wong (1996), also gives a significant underestimation of the symmetric stretching frequency. The effects of including polarizable continuum solvation or explicit hydration (admittedly with only

Table 7. Calculated Si-O-Si stretching frequencies for Si₂O₇H₆ free and hydrated.

Model and method	Calculated ν (cm ⁻¹)	Scaled ν (cm ⁻¹), using standard factors
Si ₂ O ₇ H ₆ 6-31G* HF	614	548
Si ₂ O ₇ H ₆ 6-31G* MP2	573	540
Si ₂ O ₇ H ₆ 6-311+G(2d,p) B3LYP	597	574
Si ₂ O ₇ H ₆ . . . 7H ₂ O 6-31G* HF	624	557
Exp.		≈630?

Table 8. Values for symmetric stretching frequencies in various silicates (cm^{-1}) from 6-311+G(2d,p) B3LYP calculations, rescaled to exactly fit the experimental frequency of 801 cm^{-1} in gas-phase SiF_4 , and compared with experimental values in parentheses.

Molecule	ν	$\nu \times 1.038$ (exp.)
SiF_4	772	801 (801)
Si(OH)_4	759	788 (770)
$\text{Si}_2\text{O}_7\text{H}_6$	597	620 (630?)
$\text{Si}_3\text{O}_9\text{H}_6$	606	629 (630?)
$\text{Si}_2\text{O(CH}_3)_6$	491	510 (518)

four water molecules) is also quite small, giving downward shifts (i.e., in the wrong direction compared to experiment) of less than 10 cm^{-1} compared to the free molecule values.

Accurate studies on the isoelectronic SiF_4 molecule in the gas-phase (Wang et al., 2000) have established that using methods which incorporate electron correlation more accurately than MP2 with large basis sets can give close agreement of calculated and experimental vibrational frequencies (within 10 cm^{-1} , without any scaling). This suggests that limitations in the treatment of electron correlation and in the flexibility of the basis set are probably the most important reasons for the discrepancy between calculation and experiment for Si(OH)_4 . Application of such demanding methods would presently be very difficult for Si(OH)_4 and is out of the question for $\text{Si}_2\text{O}_7\text{H}_6$. An alternative is to use a method expected to give generally good calculated frequencies like B3LYP and to scale these values to exactly match particular well determined frequencies (see below).

For $\text{Si}_2\text{O}_7\text{H}_6$ the symmetric breathing mode of the bridging O is calculated to occur at a 6-31G* HF scaled value of $\sim 550 \text{ cm}^{-1}$, considerably below the experimental feature seen at $\sim 630 \text{ cm}^{-1}$ at high T and P in aqueous solution by Zotov and Keppler (2000, 2002). This led us to explore the possibility that the feature seen by Zotov and Keppler might have the same origin as that of the so-called D2 line seen in the Raman spectrum of amorphous SiO_2 at $\sim 606 \text{ cm}^{-1}$, i.e., silicate 3-rings analogous to the molecule $\text{Si}_3\text{O}_9\text{H}_6$ (O’Keefe and Gibbs, 1984; Pasquarello and Car, 1998) We have not considered the analogous 2- and 4-rings, i.e., $\text{Si}_2\text{O}_6\text{H}_4$ and $\text{Si}_4\text{O}_{12}\text{H}_8$, since calculations such as those referenced above indicate that they do not have Raman features in the 600 cm^{-1} range.

The best computational level that we can presently use for calculation of the vibrational frequencies of all the relevant molecules is probably the 6-311+G(2d,p) B3LYP method. In many cases calculations using the B3LYP method give very accurate vibrational frequencies (Wong, 1996) and the use of the larger basis set is certainly necessary to get accurate Raman intensities (Stirling, 1996). To more closely define the calculated Raman frequencies of these molecules we have determined the scaling factor that would give exact agreement between the 6-311+G(2d,p) B3LYP calculation and the experimental gas-phase data for SiF_4 , obtaining a value of 1.038. We then used that factor to scale the calculated 6-311+G(2d,p) B3LYP values for the other species, obtaining the results in Table 8. An experimental value of 518 cm^{-1} is also available for the Si-O-Si stretch in $\text{Si}_2\text{O(CH}_3)_6$ (Hamada and Morishita, 1983) and our scaled calculated value is in good agreement. For both the dimer and the 3-ring the scaled calculated values are

quite close to the approximate experimental frequency of 630 cm^{-1} reported by Zotov and Keppler. Thus, on the basis of the match of (scaled) calculated and experimental frequencies alone, the dimer and the 3-ring seem to fit the experimental data equally well.

In Table 9 we present vibrational frequencies calculated at the 6-311+G(2d,p) B3LYP level and then scaled by 1.038, along with their Raman activities, for all the intense Raman vibrations of $\text{Si}_2\text{O}_7\text{H}_6$ to help in confirming the spectrum of this material. Only those modes with Raman activities greater than 5% of that of the Si-O-Si stretching mode (at a scaled value of 620 cm^{-1}) have been included. These are the best estimates that we can give at present for the experimental frequencies and intensities of these vibrations. These calculated frequencies are considerably different from those obtained by Zotov and Keppler (2000), which were based on a force field model partially fitted to the peak they assigned to a Si-O_{br}-Si bend and stretch at 630 cm^{-1} . They basically found one strong peak at 630 cm^{-1} and only one additional peak with a relative intensity greater than 10% of the main peak at 916 cm^{-1} . We find several peaks with intensities above 10% of the main peak in the region from 800 to 1000 cm^{-1} .

There are other changes in the Raman spectra as a function of T and P, which may correspond to additional features in the spectrum but they are rather weak, broad and unresolved. It is not clear whether they correspond to additional Raman lines for the same species giving the 630 cm^{-1} peak or arise from additional species. The energetic calculations presented in Table 4 indicate that at high temperatures the three ring species will be strongly favored by the negative -TΔS contribution. Indeed, the calculated value of ΔG_{VRT} for the formation of the 3-ring changes from -8.2 kcal/mol at 298 K to -30.9 kcal/mol at 1100 K. This is of course mainly an entropic effect, resulting from the increase in number of molecules from three in the reactants to four in the products.

4. CONCLUSIONS

Our results are consistent with the observation that the condensation dimerization of monomeric silicic acid is unfavorable at room temperature and pressure in aqueous solution but can become more favorable at high T and P, for conditions in which the dielectric constant of the aqueous fluid is low. The formation of ring silicates, such as the 3-ring molecule $\text{Si}_3\text{O}_9\text{H}_6$ is also

Table 9. Calculated frequencies (cm^{-1}) in the range 350–1000 and Raman activities ($\text{\AA}^4/\text{amu}$) for $\text{Si}_2\text{O}_7\text{H}_6$, from 6-311+G(2d,p) B3LYP calculations, using a scaling factor which exactly matches the experimental value of the symmetric stretch in SiF_4 . Only modes with activities above 5% of the 597 cm^{-1} A1 mode have been included.

ν , unscaled	Symmetry (in C_{2v})	Raman activity	ν , scaled by 1.038
391	B1	1.2	405
597	A1	14.0	620
822	A1	8.9	853
856	A1	2.8	889
936	A1	3.6	972
938	B2	1.6	974
957	A1	1.2	993
986	B1	3.2	1023

calculated to become more favorable at high T, since both changes in the VRT contributions to the gas-phase free energy and the hydration free energy become more favorable in high T, low dielectric constant environments. Calculated changes in NMR parameters from monomer to dimer are consistent with experimental data obtained at ambient T and P. Calculated changes in Raman spectra from monomer to various oligomers are consistent with observed changes at high T and P, but neither the experimental data nor the calculations can definitively distinguish between the dimer and the 3-ring trimer.

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