Theoretical Studies of the Mechanism for the Synthesis of Silsesquioxanes. 1. Hydrolysis and Initial Condensation

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Abstract: The mechanisms for the hydrolysis of $SiHCl_3$ to form $HSi(OH)_3$ and the condensations of SiH_3OH and $HSi(OH)_3$ are studied by using *ab initio* electronic structure methods including electron correlation via second and fourth order perturbation theory and coupled cluster calculations. In the gas phase, the barrier heights for the hydrolysis and silanol condensation reactions are quite high, ranging from 20 to 30 kcal/mol. The barrier for the condensation of $HSi(OH)_3$ is much smaller as a result of hydrogen bond stabilization of the transition state. Addition of just one extra water molecule is sufficient to reduce the calculated barriers to very small values or zero.

I. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) and related compounds (e.g., zeolites, metal-substituted POSS) have generated considerable interest in both the experimental and theoretical communities. For the POSS in particular, this interest derives from the wide practical uses to which these species can be applied, such as additives to improve the resistance of paints and coatings to heat and abrasion, viscosity modifiers, cross-linking agents, for advanced plastics, preceramics, and additives in a variety of pharmaceuticals.[1]

Despite the importance of these species, very little is known about the mechanism(s) by which they form. The initial step in the synthesis is typically hydrolysis of a trihalosilane ($RSiX_3$), presumably to form the corresponding trihydroxysilane,

$$R{-}SiX_3 + 3H_2O \rightarrow R{-}Si(OH)_3 + 3HX \qquad (1)$$
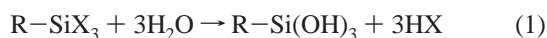
This is presumed to be followed by condensation of the trihydroxysilane,

$$R{-}Si(OH)_3 + R{-}Si(OH)_3 \rightarrow$$
$$R{-}Si(OH)_2{-}O{-}Si(R)(OH)_2 + H_2O \quad (2)$$
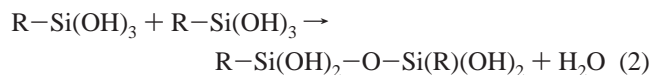
Subsequent steps involve additional condensations, ultimately building to POSS structures, such as those shown in Figure 1. Virtually nothing is known about the mechanism by which these species form, nor about the effects of the nature of R and X groups and the effects of solvent, acidic or basic media, or catalysts.

While there have been many theoretical studies of the molecular and electronic structures of both silsesquioxanes[2] and their precursors,[3] there likewise has been vritually no theoretical investigation of the potential energy surfaces for even the starting steps (1) and (2) related to the mechanism. There have been a few accurate predictions of thermochemical properties for small SiO compounds[4] and dimer hydrogen bond energies.[5] Johnson et al.[6] investigated overall energetics for the condensation of silicic acid, $Si(OH)_4$ to $(OH)_3Si{-}O{-}Si(OH)_3$ at a modest level of theory, but did not locate transition states or determine barrier heights. These authors did show the role anionic pentacoordinated silicon can play in basic media. Gordon and

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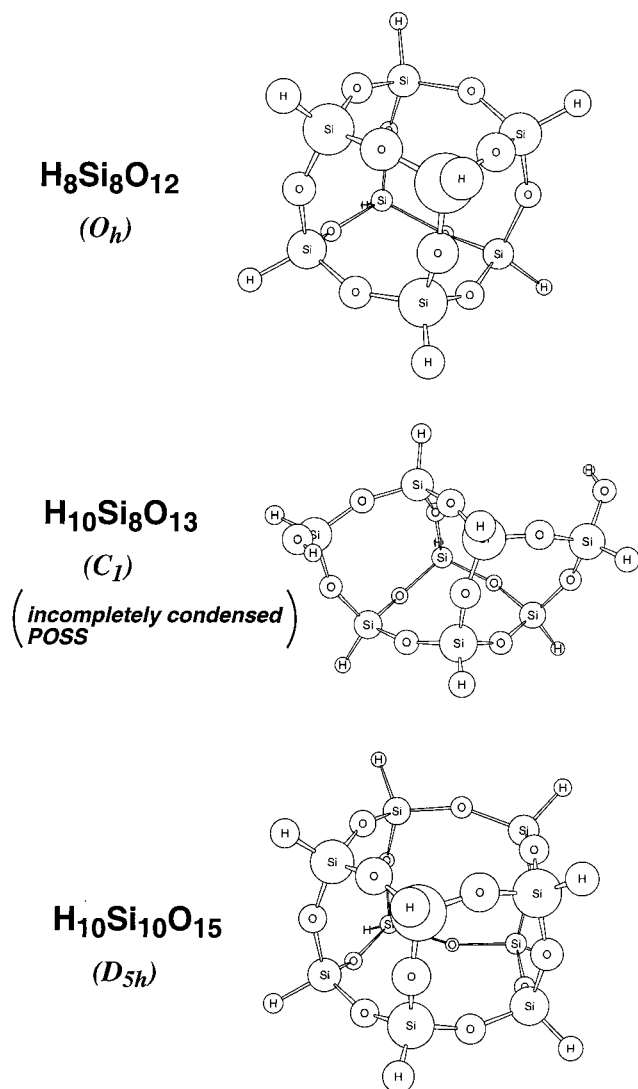
$H_8Si_8O_{12}$

(O_h)

$H_{10}Si_8O_{13}$

(C_1)

$\left(\begin{array}{l}\textit{incompletely condensed}\\ \textbf{POSS}\end{array}\right)$

$H_{10}Si_{10}O_{15}$

(D_{5h})

Figure 1. Sample structures of POSS species.

co-workers[7] investigated similar mechanisms involving penta-coordinated anionic intermediates using a combination of semiempirical and *ab initio* methods to assess both the overall energetics and the barrier heights along the competing reaction paths. Tachibana and co-workers[8] investigated the reaction of SiH_4 with SiH_3OH to produce siloxane with a modest basis set and singles and doubles configuration interaction and found a rather large (44.2 kcal/mol) barrier.

Several authors have studied the hydrogen bonding interactions between silicon−oxygen compounds and water.[9] The study that is most related to the current work is that of Xiao and Lasaga,[9d] who studied the hydrolysis of disiloxane (reverse of eq 2 for H_3SiOH) and the effect of acid catalysis on this reaction. It is quite clear that in organic systems, barriers to proton or hydrogen atom transfers can be dramatically reduced by the presence of just one or two water molecules,[10] and the effect of polar solvents on reactions such as S_N2 are well-

known,[10f] so this is clearly an important consideration in the present context.

The present paper presents a study of the reactions represented by reactions 1 and 2 as a first step in the analysis of the mechanism for the formation of POSS species. R and X are represented by H and Cl, respectively. These reactions are studied as isolated processes (that is, gas-phase reactions) and in the presence of an additional water molecule as an initial probe of the effect of aqueous solvation on the reaction energetics.

II. Computational Methods

Estimates of the structural parameters for the compounds studied in this work were obtained at the restricted Hartree−Fock (RHF) level of theory, using the 6-31G(d) basis set.[11] These geometries were then refined by using second-order perturbation theory ($MP2^{12}$) and the 6-31G(d) and 6-311G(d)[13] basis sets. Final energetics were obtained with either fourth order perturbation theory ($MP4^{14}$) or coupled cluster including single, double, and perturbatively calculated triple excitations ($CCSD(T)$,[15] with extended basis sets. The most extensive calculations have been performed for the prototypical condensation of silanol, H_3SiOH, to assess the level of theory needed for quantitative accuracy.

To determine whether a stationary point (zero gradient) on the potential energy surface is a minimum, a first-order saddle point (i.e., transition state), or a higher order saddle point, the matrix of energy second derivatives (hessian) was calculated and diagonalized. Zero, one, and >one negative eigenvalues of the hessian correspond to a minimum, transition state, and higher order saddle point, respectively. Minimum energy paths connecting transition states to their respective minima were determined by using the Gonzalez-Schlegel second-order algorithm.[16]

All of the Hartree−Fock and MP2 calculations were performed with use of the GAMESS electronic structure code,[17] while the MP4 and CCSD(T) calculations were carried out with GAUSSIAN92/DFT.[18]

III. Results and Discussion

A. Hydrolysis. The hydrolysis reactions are represented collectively by eq 1. There are actually three steps in which

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Table 1. Relative Energies (kcal/mol) for the Stepwise Hydrolysis of HSiCl₃

level	R[b]	CM1[b]	TS[b,c]	CM2[b]	P[b]
1. HSiCl₃ + H₂O → HSiCl₂OH + HCl					
RHF/6-31G*	0.0	−4.0	36.8 (21.5)	−9.0	−6.2
MP2/6-31G*	0.0	−5.9	28.0 (5.3)	−9.9	−5.3
MP4/6-31G* [a]	0.0	−5.8	29.3 (8.0)	−10.1	−5.7
2. HSiCl₂OH + H₂O → HSiCl(OH)₂ + HCl					
RHF/6-31G*	0.0	−3.4	26.9 (10.8)	−8.1	−3.2
MP2/6-31G*	0.0	−5.3	19.1 (−0.8)	−9.8	−2.9
MP4/6-31G* [a]	0.0	−5.3	20.2 (1.6)	−9.9	−3.3
3. HSiCl(OH)₂ + H₂O → HSi(OH)₃ + HCl					
RHF/6-31G*	0.0	−5.2	24.9 (9.9)	−8.3	−3.6
MP2/6-31G*	0.0	−7.0	17.8 (−0.4)	−9.8	−2.7
MP4/6-31G* [a]	0.0	−6.9	18.9 (2.0)	−9.9	−3.2

[a] Single-point energies at the MP2/6-31G* geometries. [b] R = reactant, CM1 = complex 1, TS = transition state, CM2 = complex 2, P = products. [c] Values in parentheses correspond to the presence of an additional water molecule.

successive water molecules are added to the starting material, represented here by HSiCl₃, to eliminate a molecule of HCl. The relevant structures for these three steps are shown in Figures 2a−c, respectively, and the corresponding energetics are summarized in Table 1. On the basis of the analysis for the hydrolysis of silanol (see next section), geometries obtained by using MP2/6-31G(d) followed by MP4 single point energies appear to be reasonable.

The gross features of the potential energy surfaces are the same for each step in the hydrolysis reaction: (a) the reactants silane and water form an intermediate complex (CM1), in which the water lone pair forms a weak bond with the electropositive Si, resulting in a pseudo-pentacoordinated silicon. Such addition complexes are well-known for silicon.[19] (b) The initial addition complex rearranges to a transition state (TS), in which the new SiO bond is already well formed, the new HCl bond is partially formed, and the SiCl bond is well on its way to being broken. (c) A second hydrogen-bonded complex (CM2) is formed in the exit channel, in which the fully developed hydrolysis product interacts weakly with the departing HCl. (d) The separated products are formed. Both RHF and MP2 structures are given in the figures. The correlated level of theory tends to predict a tighter interaction in both CM1 and CM2, as measured by the intermolecular distances, and tighter transition states, as measured by the partially formed and partially broken bonds to Cl. The transition states in the second and third hydrolysis steps are quite similar geometrically. The TS for step 1 appears to be somewhat tighter, in that both the forming SiO bond and the forming HCl bond are rather shorter than those in the next two steps.

The energetics for the three hydrolysis steps are summarized in Table 1. The binding energy of CM1 is underestimated by about 2 kcal/mol by Hartree−Fock, relative to the correlated levels of theory. There is very little variance between MP2 and MP4, and the use of RHF vs MP2 geometries (see Supporting Information) makes little difference. Many of the same comments can be made with regard to the second complex CM2, which is predicted to be 3−4 kcal/mol lower in energy than CM1. Note that CM1 is a bit more stable, relative to reactants, in the third hydroylsis step than it is in the first two steps. The hydrogen bond energy in the second complex is just the energy difference between P and CM2 in Table 1. This is estimated to be about 4.4 kcal/mol in hydrolysis step 1, 6.6

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kcal/mol in step 2, and 6.7 kcal/mol in step 3. So, the interaction is clearly strengthened in the last two steps; this is consistent with the relative O- - -H internuclear distances.

The barrier heights in Table 1 are rather high, although they are reduced somewhat when electron correlation is accounted for. Nonetheless, the barrier in the first step is approximately 30 kcal/mol at the MP4/6-31G(d) level of theory. The barriers in the second and third steps are about 10 kcal/mol smaller, because the transition states in these steps are stabilized by an additional hydrogen bond to Cl. Nonetheless, these barriers are still a healthy 19−20 kcal/mol. So, in the gas phase, this reaction is unlikely to proceed without a catalyst.

Since, as noted in the Introduction, the presence of even one water molecule can often have a dramatic effect on predicted barrier heights, transition states were located for each hydrolysis step, in which an additional water molecule is present in the system. The transition states for the three steps are shown in Figure 3. The additional water clearly plays the role of an intermediary in the transfer of a hydrogen atom, in much the same way as found previously for formamidine[10f] and 7-azaindole.[10g] In the first step, the water oxygen has short distances to three hydrogens, so that the transition state appears to have some zwitterionic character. Indeed, the Mulliken charge on the H₃O unit in this transition state is about +0.7. The transition states for the second and third steps are somewhat different, with the transferring hydrogen closer to its originating oxygen partner. Note also that in the second and third steps, Cl is able to hydrogen bond with two hydrogens, due to the proximity of the −OH group added in the previous step. This was noted above for the gas-phase analogues as well. Also, there are significant differences between RHF and MP2 for the internuclear distances that correspond to bonds that are being broken and formed in each step.

The effect of the additional water molecule on the hydrolysis energetics is summarized in Table 1. The water molecule dramatically reduces the predicted barrier at all levels of theory. The result is MP4 predicted barrier heights of only 8 kcal/mol for the first step and about 2 kcal/mol for the second and third steps. Although one would have to add more waters to be certain, it appears that hydrolysis in aqueous solution is an energetically feasible process.

B. Condensation. The geometries for the stationary points on the potential energy surfaces for the condensations of SiH₃OH and HSi(OH)₃ are summarized in Figures 4 and 5, respectively. For both molecules, the reaction proceeds by first forming an O−H- - -O hydrogen-bonded complex between hydroxyl groups in the reacting molecules. There is then a rearrangement through a transition state that leads to elimination of a water molecule and formation of the disiloxane. The transition state therefore involves once again the transfer of a hydrogen atom to an oxygen, so the role of the solvent is again expected to be important. This is discussed below.

The MP2 geometries in the silanol reaction (Figure 4) are predicted with both the 6-31G(d) and the 6-311G(d) basis sets. The basis set differences are fairly minor, the largest being a decrease in the hydrogen bond distance in the complex and an opening of the disiloxane Si−O−Si angle when the larger basis set is used. For trihydroxysilane (Figure 5) the intermediate contains a double hydrogen bond. Here again, the larger basis set (at the HF level of theory) predicts a shorter O- - -H hydrogen bond distance and a larger Si−O−Si angle in the siloxane product. The effect of correlation on the predicted geometries may also be seen in this figure: The O- - -H distances in the complex are shortened further, and the product Si−O−Si angle
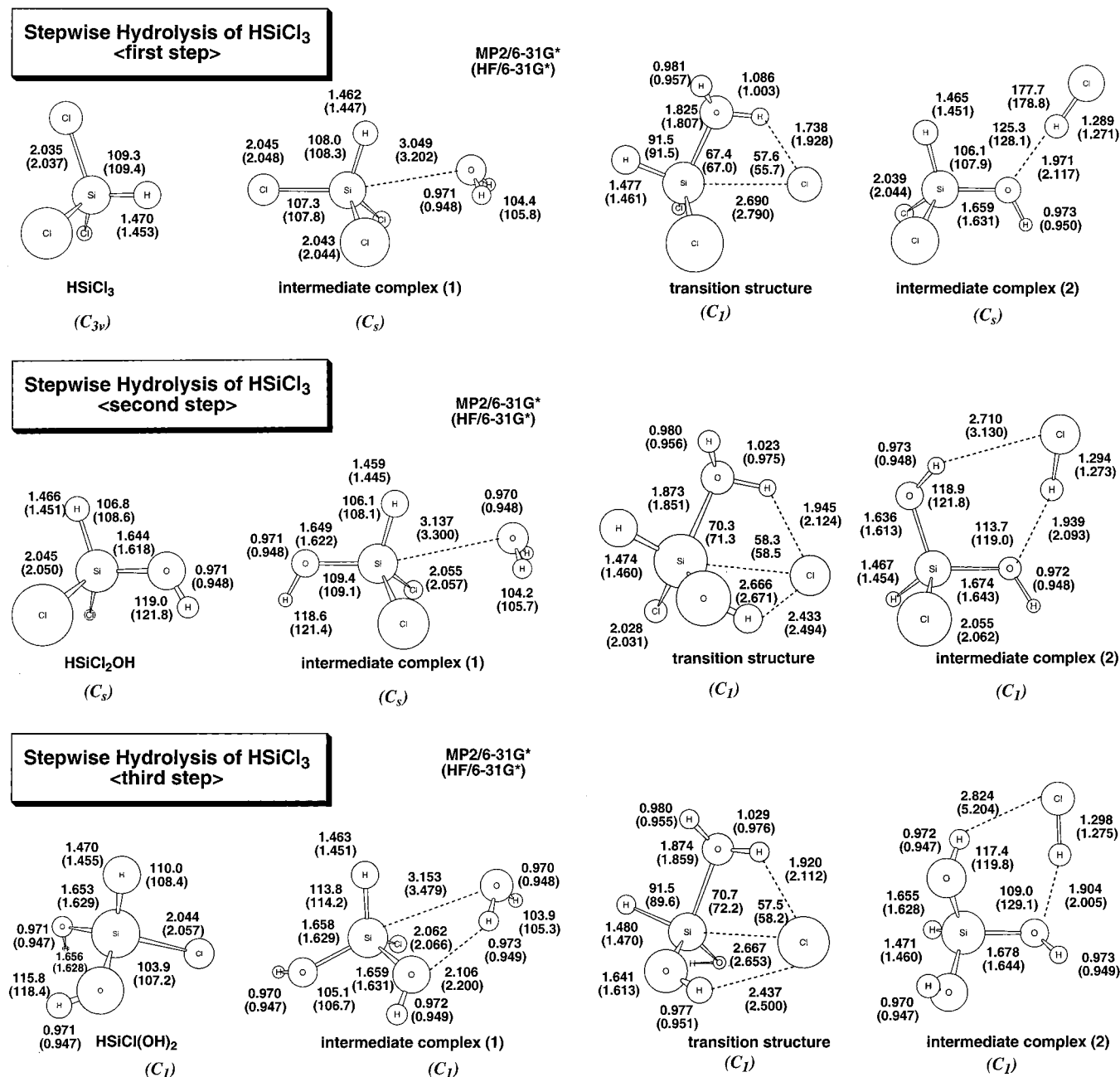
Figure 2. Stationary points for the three steps in the complete hydrolysis of Cl₃SiH. Angles are given in degrees, bond distances in angstroms.

decreases. So, improving the basis set and the level of theory have opposite effects on the Si–O–Si angle.

The energetics for the two condensation reactions are summarized in Table 2. For SiH₃OH, the overall reaction is predicted to be slightly (5–7 kcal/mol) exothermic. Variations in the magnitude of the exothermicity, as a function of basis set and level of theory, are quite small. The CCSD(T) result is in very good agreement with that obtained by combining the experimental heat of formation for water with the theoretical estimates for silanol and disiloxane made by Allendorf and co-workers.[4] Hartree–Fock theory underestimates the stability of the intermediate complex by about 2 kcal/mol. Otherwise, this species is consistently predicted to be lower in energy than the reactants by about 8 kcal/mol and lower in energy than the final products by 1–2 kcal/mol. This dimer H-bond energy is a bit higher than the MP2 value predicted by Bleiber and co-workers with a larger basis set, prior to their counterpoise correction.[5b] The barrier height for the condensation reaction is quite large,

roughly 22 kcal/mol at the highest levels of theory. This prediction is quite independent of basis set and level of theory, once electron correlation has been introduced (see Supporting Information). As is usually the case, the barrier is rather overestimated by Hartree–Fock theory. This effect of correlation was also noted by Xiao and Lasaga.[9d]

On the basis of the results for silanol discussed above, the energetics for the condensation of HSi(OH)₃ (more relevant for the formation of POSS species), also given in Table 2, have been studied at fewer levels of theory. The exothermicity for this reaction is estimated to be 10–11 kcal/mol, slightly larger than that for silanol. The stability of the intermediate hydrogen-bonded complex is considerably greater than that in the silanol reaction, since there are now two hydrogen bonds in the complex. As a result, the complex is predicted to be about 5 kcal/mol lower in energy than the final products. The effect of the additonal OH groups on the barrier height is considerable at all levels of theory. The MP2, MP4, and CCSD-
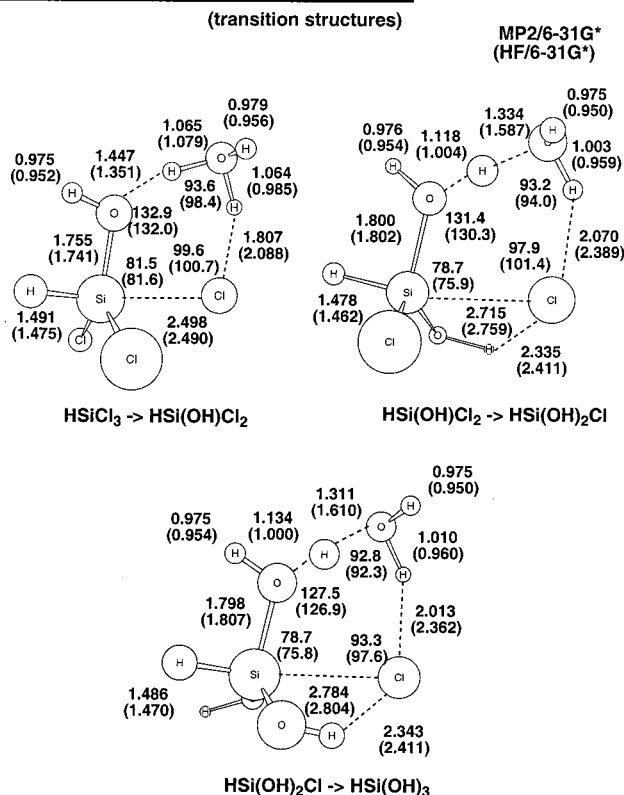
Figure 3. Transition structures for the three steps in the hydrolysis of Cl$_3$SiH in the presence of a water molecule. Angles are given in degrees, bond distances in angstroms.

(T) barriers are all reduced by about 10 kcal/mol. This is undoubtedly a consequence of the increased stability of the complex and the transition state due to the additional hydrogen bond (Figure 5).

The geometries for the intermediate complex and the transition state for the condensation of SiH$_3$OH and HSi(OH)$_3$ in the presence of an additional water molecule are shown in Figures 6 and 7, respectively. For both molecules the additional water plays the role of intermediary in the transfer of a hydrogen atom from an −OH group in one silanol to an −OH group on the partner. This enhances the stability of the transition state by forming a six-membered-ring [Si−O- - -H- - -O−H- - -O-] transition state, rather than the four-membered ring transition state in the direct (gas phase) reaction (cf. Figures 4 and 5). In the HSi(OH)$_3$ system, there is an additional stabilization due to the formation of a hydrogen bond external to the TS ring. The largest differences between the RHF and MP2 structures occur for the hydrogen bond distances. These are systematically much shorter when electron correlation is included in the geometry optimization.

The energetics corresponding to the structural information given in Figures 6 and 7 are summarized in Table 2. As suggested by the geometries, the additional water molecule has a large effect on both the stability of the intermediate complex and the associated barrier height, increasing the former by more than 10 kcal/mol and reducing the barrier by 15−20 kcal/mol. After electron correlation has been included in the calculation, there is little variation in the stability of the complex. This is predicted to be 18−19 kcal/mol for SiH$_3$OH and about 33 kcal/mol for HSi(OH)$_3$. There is somewhat more variation in the predicted barrier height as a function of basis set and level of
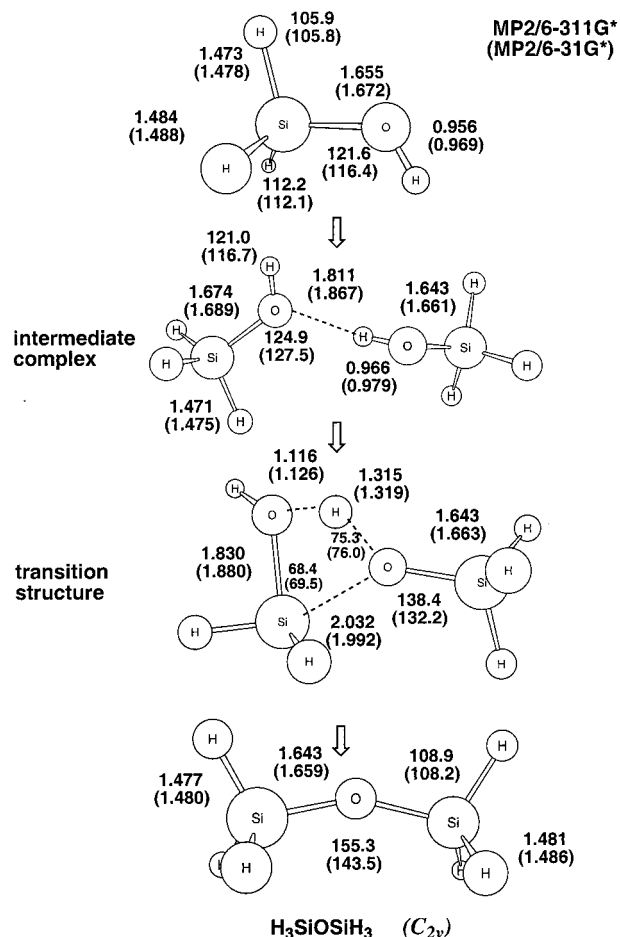

Figure 4. Stationary points for the condensation of H$_3$SiOH. Angles are given in degrees, bond distances in angstroms.

theory (see Supporting Information for more details). At the CCSD(T)/6-31G(d,p)//MP2/6-31G(d) geometries, the net barrier height for the silanol condensation is 2.7 kcal/mol, reduced from 21.9 kcal/mol without the additional water molecule. The condensation barrier for HSi(OH)$_3$ has already been shown to be much smaller than that for silanol in the absence of the extra water. When the water molecule is added, the reduction in barrier height is about the same for both molecules. Consequently, the barrier for condensation of trihydroxysilanol is reduced essentially to zero (Table 2) at all correlated levels of theory. So, it is predicted that this process proceeds without energy barrier in the presence of water. Of course, as noted in the previous discussion of the hydrolysis reaction, this conclusion is drawn for a static analysis of the potential energy surface in the presence of just one water molecule. A more general conclusion will require the addition of more water moleules and an analysis of the reaction dynamics.

IV. Summary and Conclusions

The most important result of this work is that the presence of just one water molecule can have a dramatic effect on the mechanism of POSS formation, reducing the barrier heights for both the hydrolysis and condensation steps from very large values (10−30 kcal/mol) to small or nonexistent, as has been noted before for several other reactions.[10] This is a first step in assessing the effects of solvation on the mechanism, a step

Figure 5. Stationary points for the condensation of $(OH)_3SiH$. Angles are given in degrees, bond distances in angstroms.

Table 2. Relative Energies (kcal/mol) for the Condensation of H_3SiOH and $HSi(OH)_3$

level	monomer $\times$ 2	intermediate complex[b]	transition state[b]	product
1. $H_3SiOH \times 2 \rightarrow H_3SiOSiH_3 + H_2O$				
RHF/6-31G*	0.0	−5.9 (−13.9)	35.8 (23.5)	−5.6
MP2/6-31G*	0.0	−8.2 (−19.8)	20.5 (0.4)	−4.7
MP4/6-31G* [a]	0.0	−8.1 (−19.4)	21.7 (2.9)	−4.8
MP4/6-31+G* [a]	0.0	−8.7 (−18.6)	21.8 (5.5)	−6.9
CCSD(T)/6-31G* [a]	0.0	−8.0 (−19.1)	22.4 (3.9)	−4.9
2. $HSi(OH)_3 \times 2 \rightarrow H(OH)_2SiOSi(OH)_2H$				
RHF/6-31G*	0.0	−10.4 (−23.1)	30.4 (16.7)	−7.2
MP2/6-31G*	0.0	−16.9 (−34.6)	10.9 (−9.3)	−9.9
MP4/6-31G* [a]	0.0	−16.8 (−34.1)	12.0 (−7.7)	−10.2
CCSD(T)/6-31G* [a]	0.0	−16.5 (−33.6)	12.8 (−6.6)	−10.1

[a] Single-point energies at the MP2/6-31G* geometries. [b] Values in parentheses correspond to the presence of an additional water molecule.

which needs to be followed by the addition of more water molecules and a study of the reaction dynamics.

Even without the presence of an additional water molecule, hydrogen bonding plays an important role in the mechanism. This is manifested in the reduced barrier heights in the last two steps of the hydrolysis reaction and in the condensation of $HSi(OH)_3$ vs SiH_3OH.

It also appears from this study that second-order perturbation theory is a reasonable level of theory for future investigations of the POSS mechanism. This is encouraging, since MP2 is an efficient method that lends itself well to use on parallel computers.

Figure 6. Stationary points for the condensation of H_3SiOH in the presence of a water molecule. Angles are given in degrees, bond distances in angstroms.

Figure 7. Stationary points for the condensation of $(OH)_3SiH$ in the presence of a water molecule. Angles are given in degrees, bond distances in angstroms.

Several of the issues raised in the Introduction still need to be addressed, notably, the effect of the X and R groups (Cl and

H in this work) and the effects of catalysts. These will be considered in future work.

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