Theoretical Studies of the Mechanism for the Synthesis of Silsesquioxanes. 2. Cyclosiloxanes (D_3 and D_4)

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Several possible mechanisms for the synthesis of small ring systems, $(H(OH)SiO)_n$, ($n = 3$ and 4), the three- (D_3) and four- (D_4) membered cyclosiloxanes, respectively, are investigated with ab initio molecular orbital methods including electron correlation effects. It is found that the substantial potential energy barriers that must be overcome for these species to form are reduced to nearly zero in the presence of a water molecule that represents the solvent.

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) and related compounds (e.g., zeolites and metal-substituted POSS) have attracted considerable experimental and theoretical interest for many years because of their wide variety of practical uses.[1] Although there have been many studies of their structures and properties, very little is known about the mechanism(s) by which they form. However, this information is essential for the production of new functional POSS species. The previous paper in this series presented calculated predictions for the reaction energies and barrier heights for the hydrolysis and initial condensation processes, the basic and initial steps for the synthesis of silsesquioxanes.[2] Also considered in the previous paper was the effect of the presence of a water molecule on the mechanism and the net barrier height for these first two steps. Both the second-order perturbation theory (MP2)[3] and the coupled cluster method, with single and double excitations and perturbatively included triples, CCSD(T),[4] predict that one additional water molecule dramatically reduces the barrier heights for both the hydrolysis and the condensation steps.

This work considers the subsequent condensations that result in the formation of small ring structures, $(H(OH)SiO)_n$ ($n = 3$ and 4), from monosilanes and small linear siloxanes. These small rings, together with hydroxysilanes and linear siloxanes, are the basic building blocks for the synthesis of larger cage systems. The mechanism is considered for the condensation of trihydroxysilane and disiloxane **(3)** to the three-membered ring D_3, $H(OH)SiO)_3$. Furthermore, following the previous work, the effect of an extra water molecule on this condensation reaction **(3W)** is also considered.

$$HSi(OH)_3 + H(OH)_2SiOSi(OH)_2H \rightarrow (H(OH)SiO)_3 + 2H_2O \quad \mathbf{(3)}$$

$$HSi(OH)_3 + H(OH)_2SiOSi(OH)_2H + H_2O \rightarrow (H(OH)SiO)_3 + 3H_2O \quad \mathbf{(3W)}$$

The reactant $H(OH)_2SiOSi(OH)_2H$ in (**3**) is a product of the condensation reaction considered in the previous paper.[2]

For the formation of the larger D_4 ring, $(H(OH)SiO)_4$, three mechanisms, two types of condensation **(4A−B)** and one ring expansion **(4C)**, are examined. As in the case of D_3, the effect of an extra water molecule on these condensation reactions **(4AW−4CW)** is also considered.

$$H(OH)_2SiOSi(OH)_2H + H(OH)_2SiOSi(OH)_2H \rightarrow (H(OH)SiO)_4 + 2H_2O \quad \mathbf{(4A)}$$

$$HSi(OH)_3 + H(OH)_2SiOSiH(OH)OSi(OH)_2H \rightarrow (H(OH)SiO)_4 + 2H_2O \quad \mathbf{(4B)}$$

$$HSi(OH)_3 + (H(OH)SiO)_3 \rightarrow (H(OH)SiO)_4 + H_2O \quad \mathbf{(4C)}$$

$$H(OH)_2SiOSi(OH)_2H + H(OH)_2SiOSi(OH)_2H + H_2O \rightarrow (H(OH)SiO)_4 + 3H_2O \quad \mathbf{(4AW)}$$

$$HSi(OH)_3 + H(OH)_2SiOSiH(OH)OSi(OH)_2H + H_2O \rightarrow (H(OH)SiO)_4 + 3H_2O \quad \mathbf{(4BW)}$$

$$HSi(OH)_3 + (H(OH)SiO)_3 + H_2O \rightarrow (H(OH)SiO)_4 + 2H_2O \quad \mathbf{(4CW)}$$

Because the simultaneous reaction of three trihydroxysilanes, to form the ring structures, is unlikely on microscopic kinetics grounds, such a mechanism has not been considered here.

2. Computational Methods

The geometries of all of the stationary points have been fully optimized at the restricted Hartree−Fock (RHF) level of theory using the 6-31G(d) basis set.[5] The structural refinements were carried out at the second-order Møller−Plesset (MP2)[3], and B3LYP[6] density functional levels of theory with the same 6-31G(d) basis set. All of the compounds studied here were characterized as minima or transition states by calculating and diagonalizing the Hessian matrix of energy second derivatives. Furthermore, each transition state has been connected with the corresponding minima on the appropriate potential energy surface by calculating the minimum energy path (MEP, also

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TABLE 1: Relative Energies (kcal/mol) of Several Isomers of Linear Siloxanes at Various Levels of Theory[a]

	RHF geoms			B3LYP geoms		
	RHF	MP2	MP2//MP2	B3LYP	MP2	CCSD(T)
Disiloxane ($H(OH)_2SiOSi(OH)_2H$)						
2a(C_2)[b]	0.0	0.0	0.0	0.0	0.0	0.0
2b(C_2)	3.1	5.1	5.7	4.4	5.8	5.7
Trisiloxane ($H(OH)_2SiOSi(OH)HOSi(OH)_2H$)						
3a(C_1)[c]	0.0	0.0		0.0	0.0	
3b(C_1)	3.2	5.3		5.2	6.4	
3c(C_1)	4.8	7.0		7.0	7.8	
3d(C_1)	5.3	8.7		8.5	10.1	

[a] The basis set used is 6-31G(d). [b] The total energies of 2a are −955.928 83(RHF), −956.983 38 (MP2//RHF), −956.989 43(MP2), −958.976 79 (B3LYP), −956.989 20(MP2//B3LYP) and −957.043 02-(CCSD(T)//B3LYP) au. [c] The total energies of 3a are −1395.894 57-(RHF), −1397.385 57(MP2//RHF), −1400.268 53(B3LYP) and −1397.394 94(MP2//B3LYP) au.

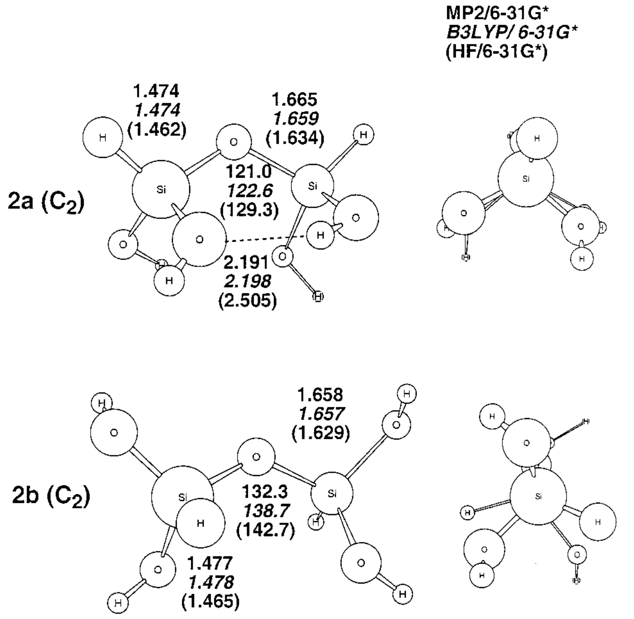


Figure 1. Two isomers (**2a** and **2b**) of disiloxane in Å and deg. Their front view (left) and the view from left side (right).

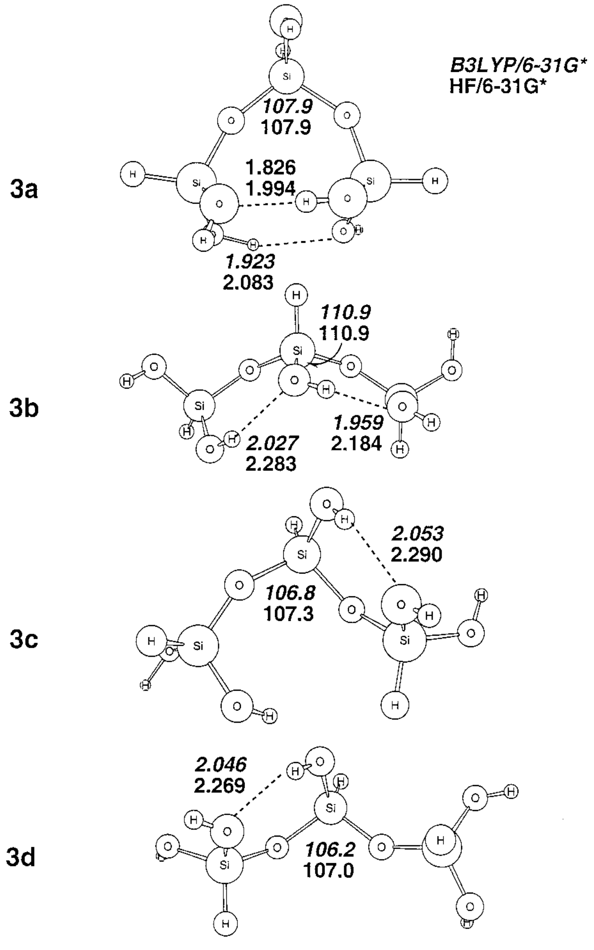


Figure 2. Four isomers (**3a**−**d**) of linear trisiloxane in Å and deg.

referred to as the intrinsic reaction coordinate, IRC). The final energetics were obtained at the MP2/6-31G(d) level of theory at the HF/6-31G(d) and B3LYP/6-31G(d) geometries and corrected with zero-point vibrational energies within the harmonic-oscillator approximation. For disiloxanes ($H(OH)_2SiOSi(OH)_2H$), coupled-cluster calculations, including single, double, and perturbative triple excitations, CCSD(T),[4] were performed with the 6-31G(d) basis set to assess the reliability of the MP2 method for the larger compounds considered here. In the previous paper,[2] several levels of theory were compared, including MP2 and coupled-cluster, CCSD(T). It was demonstrated in that paper that the MP2 method is reliable to within a few kcal/mol for both net-energy differences and barrier heights for the types of compounds and reactions considered here.

All of the Hartree−Fock and MP2 calculations were performed using the GAMESS electronic structure code,[7] whereas B3LYP and CCSD(T) calculations were carried out with GAUSSIAN98.[8]

3. Results and Discussion

Linear Siloxanes. To determine the starting points for the analysis of the potential energy surfaces, we first considered the structures and relative stabilities of the isomers of the open chain di- and tri-siloxane building blocks of the ring structures of interest. Their optimized geometries and energies are collected in Figures 1 and 2 and Table 1, respectively.

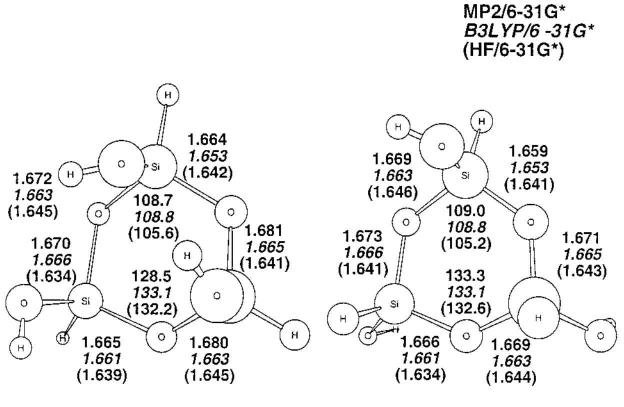
One (C_2) isomer of 1,1,2,2-tetrahydroxydisiloxane, $H(OH)_2SiOSi(OH)_2H$ (denoted **2a** in Figure 1), was determined in the previous paper to be the product of the initial condensation of 2 $HSi(OH)_3$.[2] In **2a**, the two OH groups and the one H atom centered on the first Si atom make a quasi-eclipsed conformation, relative to those on the second Si. Another C_2 isomer (**2b**) is more open with a gauche arrangement of the OH bonds. As Figure 1 shows, the O−H- - -O hydrogen bonds in **2a** are broken in **2b**. As a result, **2b** is less stable than **2a**. However, the energy difference between these isomers is small (<6 kcal/mol), as shown in Table 1, suggesting that conformational changes will readily occur at room temperature. Note that the MP2 relative energies at B3LYP geometries are very similar to those at the MP2 geometries. CCSD(T) relative energies at B3LYP geometries are also in good agreement. The geometric parameters predicted by B3LYP and MP2 are similar to each other.

Four minima (**3a**−**d**) have been located on the 1,1,2,3,3-pentahydroxytrisiloxane, $H(OH)_2SiOSiH(OH)OSi(OH)_2H$, potential energy surface (see Figure 2). As Table 1 shows, the four isomers are within ~10 kcal/mol at the MP2//B3LYP level of theory, despite their considerable difference in rotational conformation. The most stable isomer, **3a**, is stabilized by two strong O−H- - -O hydrogen bonds. From these results, it appears that the siloxane chains prefer cis conformations in order to make as many hydrogen bonds as possible. These trends should favor subsequent cyclization.

TABLE 2: Relative Energies (kcal/mol) of Several Isomers of Cyclic Siloxanes at various levels of theory[a]

	RHF	MP2//RHF	MP2	B3LYP	MP2//B3LYP
		D_3 ((H(OH)SiO)$_3$)			
D3a(C_1)[b]	0.0	0.0	0.0	0.0	0.0
D3b(C_1)[b]	0.6	0.7	2.0	0.4	0.6
		D_4 ((H(OH)SiO)$_4$)			
D4a(C_4)[c]	0.0	0.0	0.0	0.0	0.0
D4b(C_1)	2.1	4.5		4.7	5.7
D4c(C_i)	1.1	3.3	4.9	4.0	5.0
D4d(S_4)	5.0	9.8		10.0	11.9

[a] The basis set used is 6-31G(d). [b] The total energies of **D3a** are −1319.869 58(RHF), −1321.169 49(MP2//RHF), −1321.177 36(MP2), −1323.836 95(B3LYP) and −1321.174 98(MP2//B3LYP) au. [c] The total energies of **D4a** are −1759.846 17(RHF), −1761.585 72(MP2/RHF), −1761.597 04(MP2), −1765.141 58(B3LYP), and −1761.596 79-(MP2//B3LYP) au.



D3a (C_1) D3b (C_1)

Figure 3. Two isomers (**D3a** and **D3b**) of cyclotrisiloxane (D_3) in Å and deg.

Cyclic Siloxanes. Next, we considered the cyclic products of reactions (**3**) and (**4**). In Figures 3 and 4, the optimized geometries for two isomers of D_3 (**D3a, D3b**) and four isomers of D_4 (**D4a**−**D4d**) are displayed, respectively. Note that the MP2 and B3LYP geometries are generally in good agreement.

The two isomers of D_3 are very similar, with the exception that in **D3a**, all OH groups are on the same side of the ring, whereas in **D3b**, two OH groups are above and one is below the ring. Therefore, the energies (Table 2) of the two isomers are generally within 1 kcal/mol of each other. The exception is the 2 kcal/mol difference predicted at the MP2//MP2 level of theory. The rings themselves are not planar, in contrast with the previously reported planarity of the ($H_2SiO)_3$ ring.[9]

For D_4 (Figure 4) four isomers have been found. As for D_3, the lowest energy isomer (Figure 4, **D4a**) is the one that has all four of the OH groups "above" the ring, whereas the highest energy isomer (**D4d**, by 12 kcal/mol) is the one that has OH groups alternating above and below the ring. As one would expect from the previous discussion of the acyclic disiloxanes, **D4a** is stabilized by the presence of strong O−H- - -O hydrogen bonds. This is in agreement with the experimental result of Unno and Matsumoto who have obtained only the all-cis isomer of tetrahydroxy-tetraisopropylcyclotetrasiloxane.[10] The next most stable isomer, **D4c** has two hydrogen bonds with short distances (Figure 4). For the case in which all of the hydrogen atoms attached to silicon atoms are replaced by OH groups, the D_4 structure becomes C_i.[11] Note that the all-cis forms are convenient for the subsequent face-to-face condensation of two D_4's to form the cage (T_8) structures. Therefore, OH groups are found to play a very important role, not only for determining the structures of siloxanes, but also with regard to their influence on the reaction mechanism for the synthesis of silsesquioxanes. Because of geometric constraints, hydrogen bonding is less important in determining the relative energies of the D$_3$ isomers. In general, the MP2//B3LYP and MP2//MP2 energies are in reasonable, although imperfect, agreement for the smaller compounds studied (Tables 1-2). The results presented below are therefore at the former level of theory, to reduce computational expense.

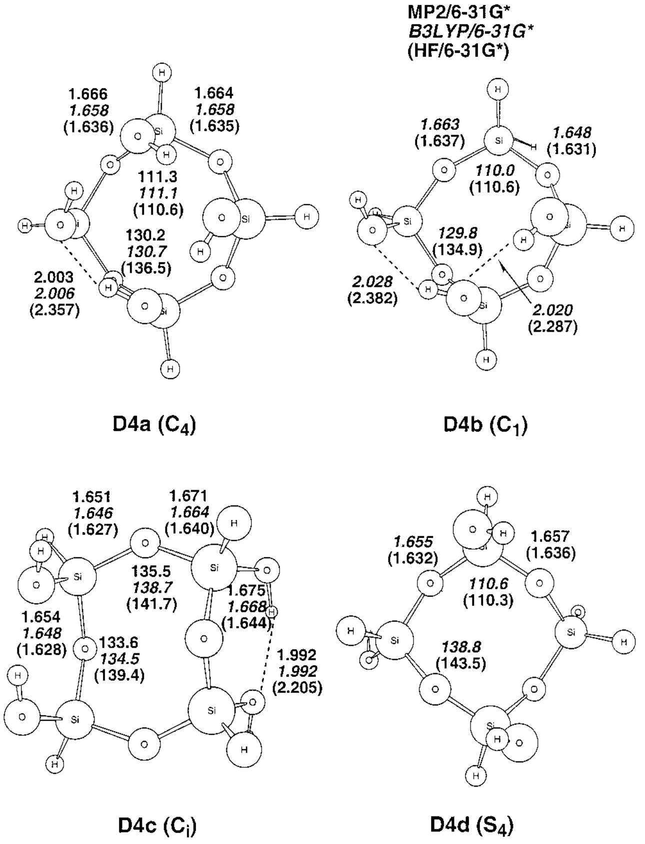


Figure 4. Four isomers (**D4a**−**d**) of cyclotetrasiloxane (D_4) in Å and deg.

D_3 Formation. Next, we considered the stepwise (1 + 2) reaction mechanism for the formation of D_3 summarized in reaction (**3**). The geometries for the stationary points on the potential energy surface are displayed in Figure 5. In the initial step, HSi(OH)$_3$ and tetrahydroxy disiloxane form a hydrogen-bonded complex (**cm1**). This process is downhill in energy by ∼17 kcal/mol (MP2), with no intervening barrier. The complex eliminates one water molecule to form intermediate trisiloxane **3a** via a condensation transition state **ts1**. The transition state is uphill by ∼28 kcal/mol, but the complex **cm2** is still nearly 11 kcal/mol below that of the starting reactants at the MP2 level of theory. However, **ts1** is 12 kcal/mol above that of the reactants. Subsequently, the final product, D_3 (Figure 5, **D3a**) is formed through an intramolecular condensation of **3a** and elimination of the second water. This second transition state **ts2** has an even larger MP2 barrier of 31 kcal/mol, 20 kcal/mol above that of the reactants. The net reaction is predicted to be slightly endothermic. The second condensation is the rate-determining step, and the calculated barrier is too high for this reaction to occur at room temperature. The energy barrier for the first transition state is very similar to that found for the condensation of 2 HSi(OH)$_3$ at MP2/6-31G(d) in the previous work. This suggests that the energy barrier for this type of

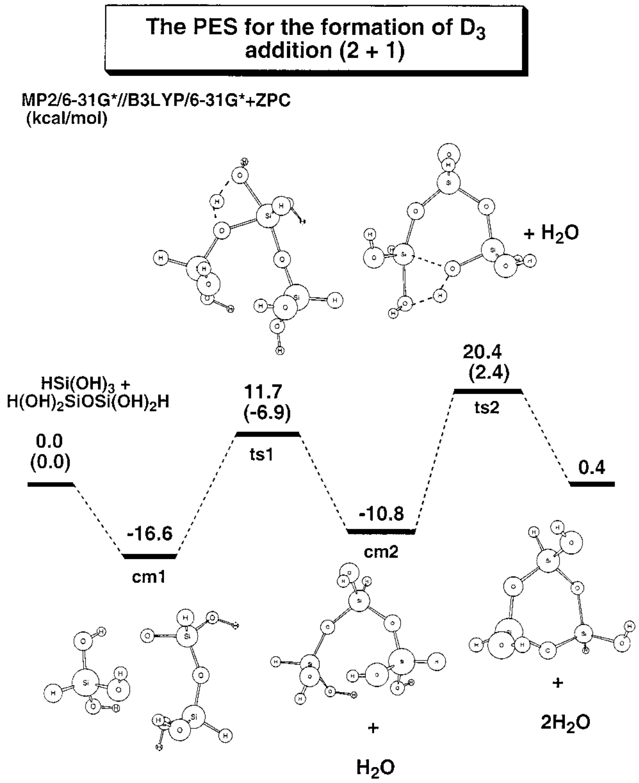


Figure 5. Potential energy surface (kcal/mol) and stationary points for the condensation of disiloxane and $HSi(OH)_3$. The values in parentheses are for the water-assisted case.

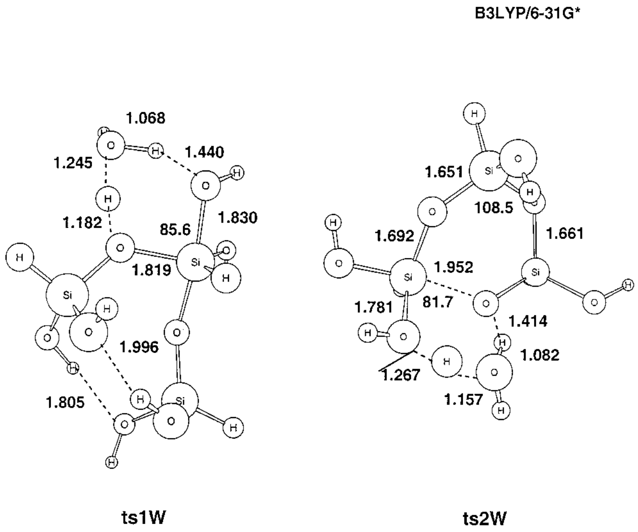


Figure 6. Transition structures for the condensation of disiloxane and $HSi(OH)_3$ in the presence of an extra water molecule.

condensation depends primarily on the local structures rather than the size of siloxanes.

In the previous study,[2] it was shown that the presence of just one water molecule can reduce the barrier height for the condensation of $HSi(OH)_3$ by ~30 kcal/mol, from a large value to nearly zero. Therefore, the effect of an extra water molecule on the two transition states in Figure 5 has been investigated. The corresponding transition structures (**ts1W** and **ts2W**, corresponding to **ts1** and **ts2**, respectively) are shown in Figure 6. Their six-membered ring structures are very similar to those of the transition structure for the condensation of $HSi(OH)_3$.[2] The corresponding MP2 energy barriers with zero-point corrections are −6.9 and 2.4 kcal/mol (listed in Table 3, and in parentheses in Figure 5), respectively. Clearly, a single water molecule also has a dramatic effect on the energetics of the formation of D3. The more severe geometry constraint may be the reason that there remains a small barrier in the second transition state.

TABLE 3: Energies (kcal/mol)[a] of Stationary Points for the Reactions 3(W) and 4A(W)−4C(W) Relative to Their Reactants

	3(W)	4A(W)	4B(W)	4C(W)
CM1	−16.6	−15.5	−18.5	−18.1
TS1	11.7	12.4	10.1	12.7
	(−6.9)	(−10.1)	(−13.5)	(−9.5)
CM2	−10.8	−12.5	−11.3	−22.5
TS2	20.4	18.0	19.2	8.0
	(2.4)	(−2.3)	(−1.0)	(−12.3)
P	0.4	−8.8	−7.5	−18.8

[a] MP2/6-31G*//B3LYP/6-31G* + ZPC energies. [b] Values in parentheses correspond to the case with extra water.

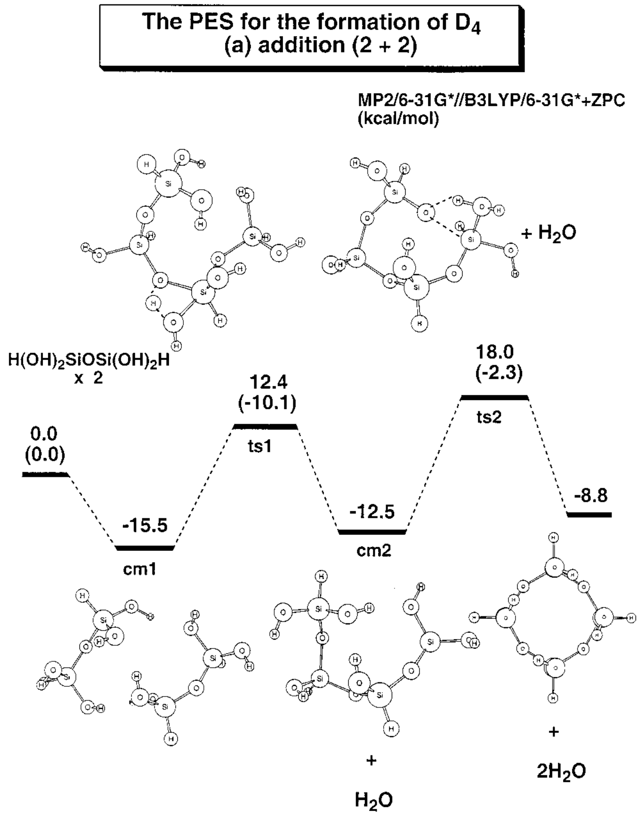


Figure 7. The potential energy surface (kcal/mol) and stationary points for the condensation of two disiloxanes. The values in parentheses are for the water-assisted case.

D*$_4$ *Formation. We considered the three mechanisms referred to in the Introduction as **4A**−**C**. The schematics of the potential energy surfaces for these three reactions are shown in Figures 7−9. It is assumed that the final ring-closing step is common to the two addition reactions, **4A** and **4B**.

The (2 + 2) condensation (**4A**) proceeds in a manner similar to that of D_3, see Figure 7. A hydrogen-bonded complex (**cm1**) is formed at first, downhill by 16 kcal/mol at the MP2 level of theory, with no intervening barrier. The first condensation reaction then proceeds via transition-state **ts1** to a second complex (**cm2**).[12] The barrier for this slightly endothermic step is 28 kcal/mol, with **ts1** lying 12 kcal/mol above that of the reactants. The final step for the formation of D_4 is the ring closing of the linear tetrasiloxane (**cm2**) via a second transition state **ts2**. This second barrier is more than 30 kcal/mol (18.0

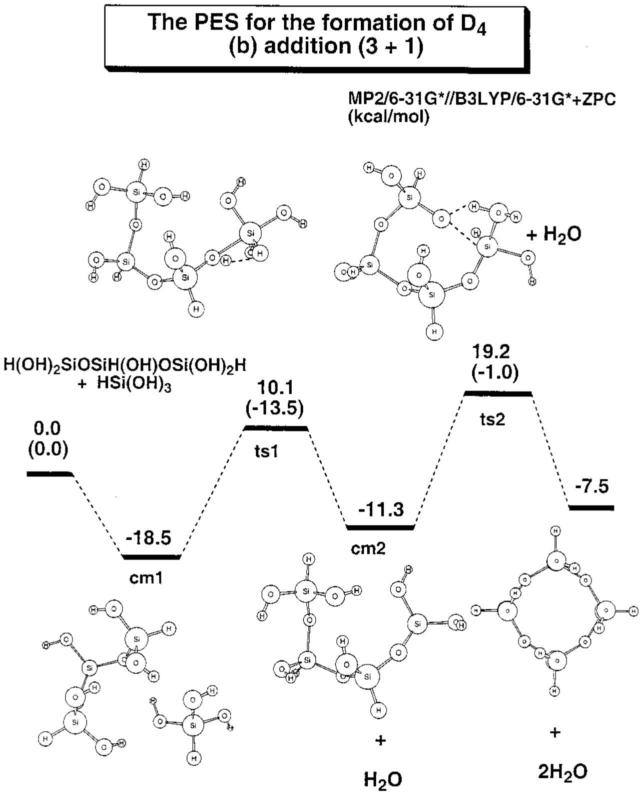


Figure 8. The potential energy surface (kcal/mol) and stationary points for the condensation of trisiloxane and $HSi(OH)_3$. The values in parentheses are for the water-assisted case.

kcal/mol above that of the reactants). So, even though the two complexes and the final product are all below the starting reactants, there is a net energy penalty of 18.0 kcal/mol for the reaction to occur, with the bottleneck occurring at the ring-closure step, similar to the mechanism for the formation of D_3. The mechanism for the (1 + 3) condensation (**4B**), summarized in Figure 8, is quite similar. The ring-closure step is again the bottleneck for the overall reaction. The ring expansion mechanism (**4C**, Figure 9) is similar to 4A and 4B. The net MP2 energy requirement for this mechanism, 12.7 kcal/mol, is similar to those of the two alternative, stepwise condensation mechanisms.

The high barriers for the ring-closure steps are likely to be caused by ring strain in the corresponding transition structures. The net barrier for this step is similar (18 vs 19 kcal/mol) in mechanisms **4A** and **4B**. The ring-closure energy barrier for the formation of D_3 is slightly higher. The smaller energy barrier for the first condensation steps in mechanisms **4A** and **4B** are due to stabilization from hydrogen-bond formation.

Because the predicted barrier heights for all three of the mechanisms are of the same order of magnitude as that for the formation of D_3, it is anticipated that the addition of a water molecule will likewise dramatically reduce the net barriers. The water-assisted transition states for the formation of D_4 are shown in Figure 10 (**ts1AW**, **ts2AW**, **ts1BW**, and **tsCW**; recall that it is assumed that **ts2AW** and **ts2BW** are the same). The transition structures are essentially the same as those of D_3 and the previously studied smaller system[2]. Furthermore, the effect of a water on the barriers is very large, as expected (see Table 3). In the presence of the extra water, all barriers vanish at the MP2//B3LYP level of theory.

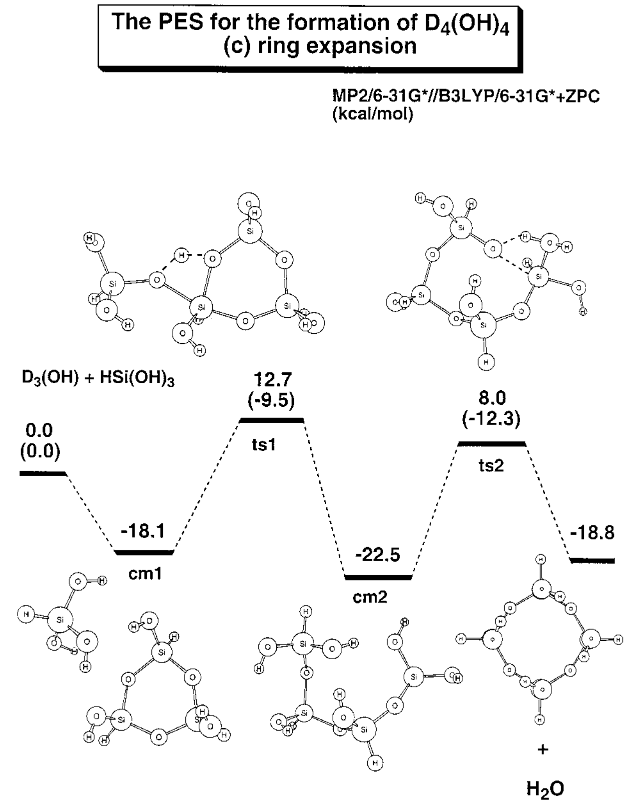


Figure 9. The potential energy surface (kcal/mol) and stationary points for the ring expansion by cyclotrisiloxane (D_3) and $HSi(OH)_3$. The values in parentheses are for the water-assisted case.

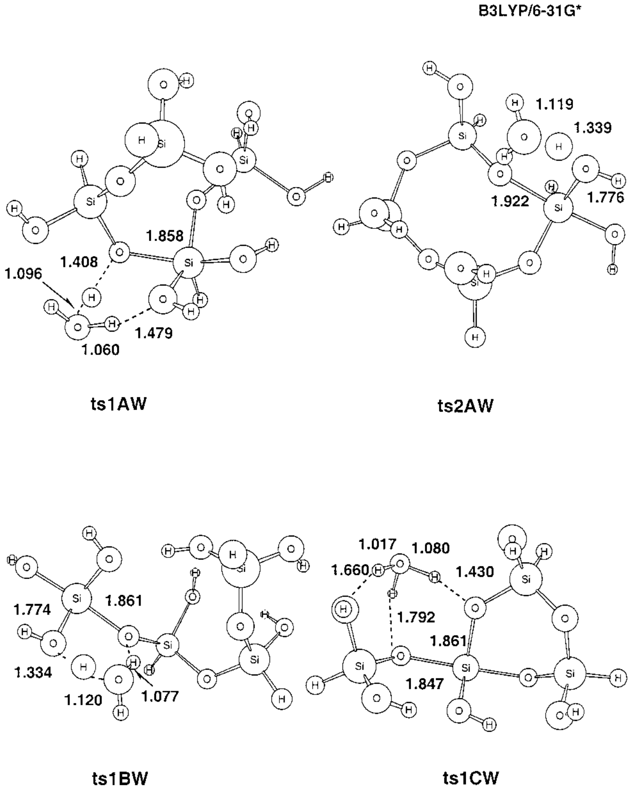


Figure 10. Transition structures for D_4 formation in the presence of an extra water molecule.

4. Summary and Conclusions

In the present work, the reaction mechanisms for the formation of cyclotrisiloxane (D_3) via a (1 + 2) condensation and cyclotetrasiloxane by (2 + 2) and (1 + 3) condensations, as well as ring expansion, have been investigated. In the gas phase, the net energy barrier for the ring expansion is slightly higher than those for the mechanisms for both D_3 and D_4 formation, although the energy differences are quite small. All of the net barriers are found to be substantial. Of course, it is possible that there are other conformations for both minima and transition structures with similar energies,[12] but it is unlikely that these will have significantly different energetics.

As has been found in several other theoretical studies, including the first paper in this series, the presence of an additional water molecule dramatically reduces the barrier to zero, or nearly zero. This is accomplished by the water molecule's action as a conduit for proton transfer, thereby stabilizing the transition state through hydrogen bonding and reduced strain. Of course, this observation is only *suggestive* of the effect of a solvent. However, it is consistent with the observed very rapid formation of POSS species in solution.[13]

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