Mechanism of the Acid-Catalyzed Si−O Bond Cleavage in Siloxanes and Siloxanols. A Theoretical Study

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Theoretical ab initio calculations were carried out to simulate the hydrolysis of the siloxane bond under neutral and acidic conditions. The most important factors reducing the energy barrier of the reaction are the protonation of the siloxane oxygen (acid catalysis) and the basic assistance to the nucleophile (responsible for withdrawal of the proton from a nucleophile). The basic assistance may be effectively accomplished by hydrogen bond complexes, which help to transfer a proton from the nucleophile to the leaving group. Such complexes may consist of water, silanol, and acid. Solvation lowers the barrier of acid-catalyzed hydrolysis, due to better stabilization of the charged transition states. The enhanced reactivity of the terminal siloxane bond in siloxanols is connected partly with the ability of the SiOH group to participate in hydrogen bond structures facilitating the intramolecular proton transfer to the siloxane oxygen.

Introduction

Acid-catalyzed condensation of silanol groups is the most important reaction leading to the formation of the siloxane bond.[1] This reaction is widely used in technology for the synthesis of various macromolecular siloxane architectures, such as linear siloxane polymers and copolymers (silicones),[1b,c] silsesquioxanes,[2] and silica networks and glasses.[3] Therefore, the mechanism of this reaction has been studied intensively.[4] Recently, along with the development of computational methods, it has also attracted considerable interest of theoreticians.[5]

Kinetic studies showed that in acidic media silanol condensation is a set of elementary equilibrium reactions (eqs 1−4).[6] Formation of hydrogen bond complexes (eq 4) strongly affects the overall equilibrium position by decreasing the effective concentrations of acid, silanol, and siloxane species. Therefore, the equilibrium of condensation/siloxane bond cleavage is very sensitive to the proton donor−acceptor properties of the medium as well as to the presence of water or other additives capable of forming strong hydrogen bonds.[6]

$$\equiv SiOSi\equiv + HA \rightleftharpoons \equiv SiA + HOSi\equiv \quad (1)$$

$$2 \equiv SiOH \rightleftharpoons \equiv SiOSi\equiv + H_2O \quad (2)$$

$$\equiv SiA + H_2O \rightleftharpoons \equiv SiOH + HA \quad (3)$$

$$HA + Base \rightleftharpoons A\text{-}H\cdots Base,\ \text{where Base} = H_2O, \equiv SiOH, HA, \equiv SiA \quad (4)$$

The reactions of the SiO bond cleavage by acid (eq 1) or water (reverse reaction in eq 2) play an important role in all acid-catalyzed processes leading to polysiloxanes. They significantly affect the polycondensation course, causing depolymerization with production of low molecular weight byproducts. Particularly fast is the cleavage of the siloxane bond geminal to a silanol group (eq 5), resulting in the exchange of the terminal siloxane unit between polymer molecules.[4d−f] This reaction is responsible for degradation of silicones in the atmosphere, in the soil, and also in biological systems (eq 6).[7]

The cleavage of the siloxane bond is a crucial reaction in the ring-opening polymerization of cyclosiloxanes. Thus, breaking of the monomer ring is involved in both the initiation and the propagation steps, while the splitting of the Si−O linkage in the polymer chain is

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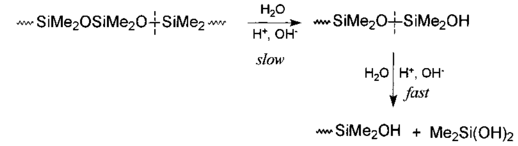
$$\sim R_2SiO\vdots\mathbf{R_2SiO}\text{-}H + H\text{-}OSiR_2OSiR_2\sim \xrightarrow{H^+, OH^-} \sim R_2SiOH + H\text{-}\mathbf{OSiR_2}\text{-}OSiR_2OSiR_2\sim \quad (5)$$



(6)

responsible for depolymerization. Studies of the initiation of ring-opening polymerization of cyclosiloxanes by protic acids demonstrated also the essential role of hydrogen bond complexes in the kinetics of this process. In anhydrous conditions, the siloxane bond is effectively cleaved by acid homo-complexes comprising of three or four molecules of acid.[8] On the other hand, addition of a small amount of water strongly accelerates the polymerization of hexamethylcyclotrisiloxane, $(Me_2SiO)_3$, by up to 100 times.[9] On the basis of the kinetic observations, the mechanism for the cleavage of the SiO bond was proposed, assuming that acid or acid−water associates consisting of three or four molecules are the true reactive species in the acidolysis reaction (Scheme 1, **a** and **b**, respectively).[8]

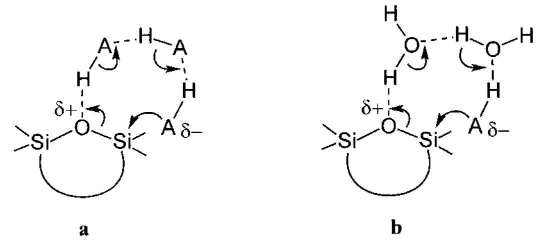
Theoretical studies of the mechanism of silanol condensation confirmed the role of water in lowering the activation energy of the condensation/hydrolysis reactions.[5] Water stabilizes the transition states for bond cleavage/formation through hydrogen bonding, reducing angular strain, and participating in proton transfer. Although the computational results apply strictly to the gas phase, the qualitative agreement with the kinetic observations for reactions in solution proves the usefulness of theoretical methods in mechanistic studies of these processes.

Since silanol condensations are always conducted in the bulk or in solution, the reaction mechanism in the condensed phase is of particular interest. No evidence has been provided that condensation of silanols, even in the case of highly reactive silanepolyols, $R_{4-n}Si(OH)_n$, $n > 1$, may proceed in the complete absence of a catalyst.[1,4a] The presence of an acid or a base is necessary for the reaction to proceed. Since the kinetic system is very complex and the data are difficult to interpret unequivocally, theoretical methods may help to get closer insight into the structures of transition states as well as to understand the role of hydrogen bond complexes in the hydrolysis of a siloxane bond.

The present work describes ab initio and density functional theory (DFT) calculations of the hydrolytic cleavage of the siloxane bond in simple disiloxane, $H_3SiOSiH_3$, and disiloxanol, $H_3SiOSiH_2OH$, by water clusters, the main motivation being to gain a deeper understanding of the mechanism of proton transfer and of the competition of silanol (Si−OH) and siloxane (Si−OSi) bond cleavage under acidic conditions.

Computational Methods

Scheme 1



Ab initio calculations were performed using the Gaussian 98 series of programs.[10] Geometry optimizations were performed at the restricted Hartree−Fock (RHF) level of theory, using the 6-31G* basis set. Vibrational frequencies at the HF/6-31G* level were computed for all species to characterize them as minima, transition structures, or higher order saddle points on the potential energy surface. In cases of doubt, a potential energy scan and IRC calculations were performed to verify that the transition structures are indeed the first-order saddle points on the reaction pathway that have only one imaginary frequency mode. Enthalpies and Gibbs free energies at 298 K were calculated using the ideal gas approximation as implemented in Gaussian 98. Final energies were obtained at the correlated level using the fourth-order perturbation theory, MP4(SDTQ)/6-31G*,[11] and the hybrid density functional B3LYP/6-311+G(2d,p) method.[12,13] The energies obtained by these methods are referred to in the text as HF, MP4, and DFT, respectively. The energy barriers of the reactions of interest are reported relative to the energies of the reactive complexes rather than to the free substrates, since these values give a better idea of the energy barriers in solution, where reagents are strongly solvated and associated through hydrogen bonds. The effect of the solvent on the reaction energetics was evaluated using the SCRF (PCM) method.[14] Analysis of orbital interactions was performed using the natural bond orbital (NBO) theory.[15] The energies associated with specific orbital interactions were calculated with the NBO deletion procedure as the difference between the total SCF energy and the energy obtained by deleting the off-diagonal Fock matrix elements corresponding to the interacting bond−antibond pair of interest.[15]

Results and Discussion

Since previous calculations on the condensation/hydrolysis reactions of silanols were performed for different model systems and at different levels of theory,[5] quantitative comparison of the various results is difficult. Therefore, it was necessary to perform

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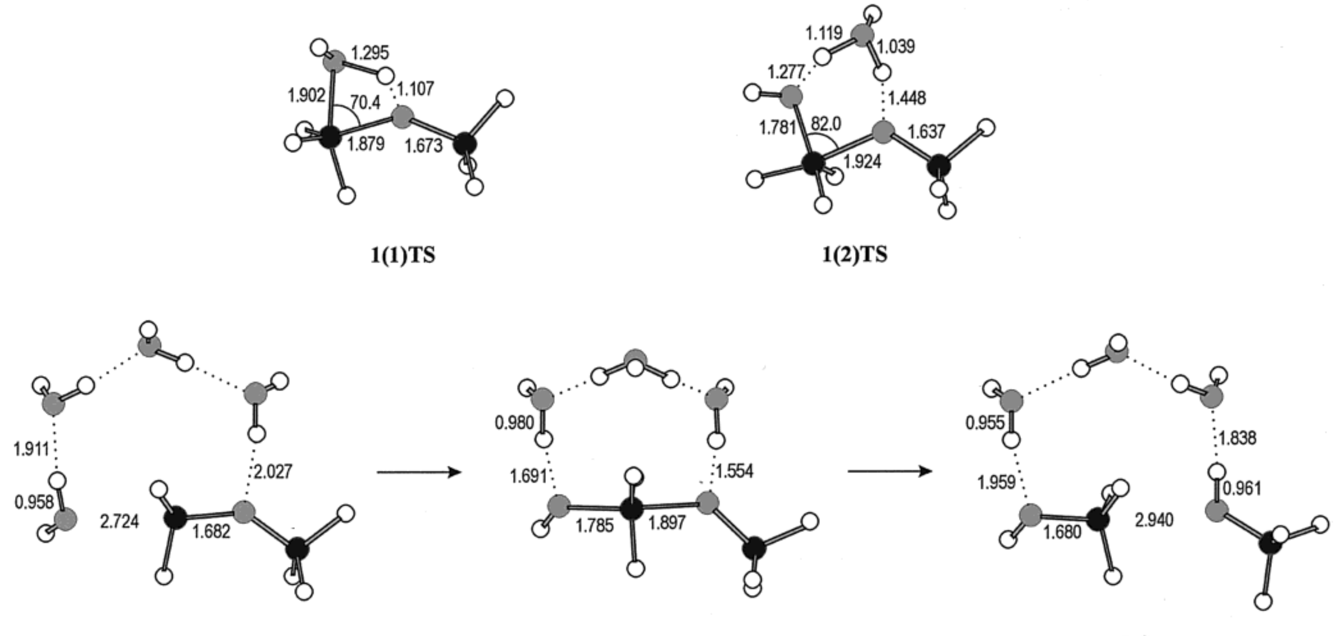
Scheme 2. Transition State Structures for Hydrolysis of Disiloxane 1 by a Single Water Molecule, 1(1)TS,[5b] and by a Water Dimer, 1(2)TS;[5b] Structures of the Reactive Complex, 1(4)RC, Transition State, 1(4)TS, and Product Complex, 1(4)PC, for Hydrolysis of 1 by a Water Tetramer



1(1)TS **1(2)TS**

1(4)RC **1(4)TS** **1(4)PC**

systematic calculations of the hydrolysis of the Si−O bond by water clusters $(H_2O)_n$, $n = 1-4$, under neutral conditions and in the presence of acid protonating the siloxane. This was accomplished using the simplest disiloxane, $H_3SiOSiH_3$ (**1**). The effect of a geminal OH group on the energetics of siloxane hydrolysis was studied using the model disiloxanol $H_3SiOSiH_2OH$ (**2**).

Siloxane Bond Cleavage in $H_3SiOSiH_3$ (1). Although experimental data show that hydrolysis of siloxanes under neutral conditions is extremely slow, it is interesting to compare the theoretical results for the neutral reaction with the acid-catalyzed one. The hydrolysis of **1** was previously investigated theoretically by Xiao and Lasaga,[5a] while the reverse reaction, the condensation of silanol, H_3SiOH, under neutral conditions, without water and in the presence of one water molecule, was studied theoretically by Kudo and Gordon (eq 7).[5b]

$$H_3SiOSiH_3 + (H_2O)_n \rightarrow 2\ H_3SiOH + (H_2O)_{n-1} \quad (7)$$

We used the HF/6-31G* stationary geometries reported by these authors to recompute the energies at the levels of theory applied in this study. The reactions involve the front-side attack of monomeric or dimeric water at silicon and proceed with retention of configuration at Si. The key step in the process is the transfer of a proton from the water molecule, acting as a nucleophile, to the leaving group.[5a] Consequently, a negative charge develops on the nucleophile's (water) oxygen, the distance to silicon shortens, and the linkage between silicon and oxygen in the siloxane loosens. On the other hand, the interaction with the proton stabilizes the leaving group. For geometrical reasons, the front-side attack is energetically favored in hydrolysis of siloxane by the water monomer or dimer.[5a−c] In hydrolysis by one water molecule, the proton is transferred in the TS (**1(1)TS** in Scheme 2) synchronously from the nucleophile (water) to the leaving group (silanolate).[16] In hydrolysis by a water dimer, the proton withdrawal from the attacking nucleophile is in a TS (**1(2)TS** in Scheme 2) much more advanced than the proton transfer to the leaving group. The change of the nucleophile from a water monomer to a dimer lowers the activation energy for siloxane hydrolysis (at MP4 and DFT) by approximately 10 kcal/mol, from ca. 34 kcal/mol for H_2O to 24.5 kcal/mol for $(H_2O)_2$ (DFT), relative to the reactive complex (Table 1). The HF activation energies are ca. 10 kcal/mol higher than the energies obtained at correlated levels, as discussed previously.[5b]

The backside attack of water on the silicon atom is preferred if the geometry of the reactive complex allows an efficient cooperative hydrogen bond system.[17] This is the case for hydrolysis of the siloxane bond by a water tetramer. The reaction proceeds with formation of a cyclic hydrogen bond complex. The structures of the early reactive complex, **1(4)RC**, the transition state, **1(4)TS**, and the product complex, **1(4)PC**, are shown in Scheme 2. While the activation energy for hydrolysis of **1** decreases by ca. 10 kcal/mol on changing the nucleophile from H_2O to $(H_2O)_2$, the calculated energy barrier for a water tetramer is only 2 kcal/mol lower than that for the dimer (Table 1). Thus, increasing the number of water molecules participating in hydrolysis

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[16] All species are denoted according to the following convention: the first number refers to the siloxane model compound (**1** for disiloxane, **2** for disiloxanol, **3** for 1,1-dimethylsiloxane, and **4** for 1,1-dimethyldisiloxan-1-ol); an H suffix denotes a protonated siloxane species; the second number in parentheses is the number of water molecules involved in the reaction; **RC**, **TS**, **PC** denote the reactive (early) complex, transition state, and the product complex, respectively. Black, dark gray, gray, and white circles in schemes correspond to Si, C, O, and H atoms, respectively. Only the selected bonding parameters are shown. Full structural information is given in the Supplementary Information.

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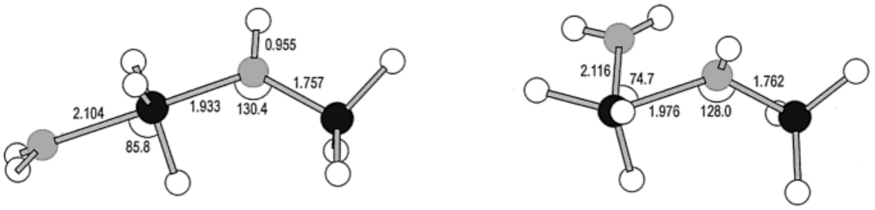
Scheme 3. Structures of the Complex Resulting from the Back-Side Attack, 1H(1)RC-b, and of the Transition State for the Front-Side Attack, 1H(1)TS-f,[5a] of Water on the Protonated Disiloxane 1H



1H(1)RC-b **1H(1)TS-f**

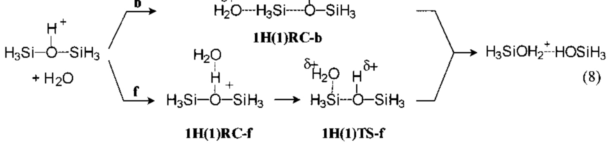
Table 1. Calculated Relative Energies (kcal/mol) for the Hydrolysis of Disiloxane (1) and Protonated Disiloxane (1H) by Water Clusters $(H_2O)_n$, $n = 1, 2, 4$

n	level[a]	substrates	RC	TS	PC	products
		$\mathbf{1} + (H_2O)_n \rightarrow 2\ H_3SiOH + (H_2O)_{n-1}$				
1	HF	2.9	0	46.0	2.6	
	MP4	6.1	0	33.7	2.6	
	DFT	2.9	0	33.9	0.2	
2	HF	4.6	0	39.4	2.0	
	MP4	9.6	0	24.3	2.3	
	DFT	4.0	0	24.7	−0.2	
4	HF	−0.8	0	39.2	2.5	
(Scheme 2)	MP4	3.6	0	22.4	2.8	
	DFT	−0.9	0	23.0	1.2	
		$\mathbf{1H} + (H_2O)_n \rightarrow H_3SiOH_2^{(+)} + H_3SiOH + (H_2O)_{n-1}$				
1	HF	22.2	0 (1.4)[b]	24.5[c]	3.6	27.1
(Scheme 3)	MP4	28.5	0 (3.1)[b]	26.3[c]	6.5	32.8
	DFT	19.9	0 (0.5)[b]	21.9[c]	−0.1	26.1
4	HF	37.2	0 (1.5)[d]	10.0	3.0	
(Scheme 4)	MP4	43.5	0 (1.2)[d]	8.5	5.6	
	DFT	34.6	0 (1.6)[d]	4.5	−2.7	

[a] HF = HF/6-31G*; MP4 = MP4/6-31G*//HF/6-31G*; DFT = B3LYP/6-311+G(2d,p)//HF/6-31G*. [b] In parentheses are given relative energies for complex **1H(1)RC-b** resulting from back-side attack. [c] Transition state resulting from front-side attack (**1H(1)TS-f**).[5a] [d] In parentheses are given relative energies for complex **1H(4)RC2**.

above 2 does not significantly affect the energy barrier for **1**. Even for a water tetramer, the MP4 and DFT barriers for hydrolysis of **1** are still high, 22−23 kcal/mol, although further lowering may occur when larger water clusters are involved. Nevertheless, neutral hydrolysis of siloxanes is very slow, and the theoretical results are consistent with observations.[7]

Hydrolysis of the protonated disiloxane $H_3SiO(H^+)SiH_3$ (**1H**) proceeds according to a somewhat different mechanism (eq 8). Xiao and Lasaga studied the mechanism theoretically implying the front-side attack of a water molecule.[5a] In the TS the motion along the reaction coordinate was dominated by the formation of the new SiO bond and the rupture of the original bond, in contrast to neutral hydrolysis, which was determined by proton transfer. At MP2/6-31G* the TS lies only about 2 kcal/mol above the substrates (**1H** + H_2O).[5a] However, the energy barrier, compared to the reactive complex (**1H(1)RC-f** in eq 8), is ca. 23 kcal/mol. Because the protonated siloxane oxygen is unable to interact efficiently with the electrophilic part of the nucleophile (a proton in the case of water), the front-side attack (**f**) proposed by Xiao may not be favorable. We thus examined the mechanism, in which the nucleophile approaches the protonated siloxane (path **b** in eq 8) from the direction opposite the leaving group, leading to inversion of configuration at silicon. This approach results in the formation of a stable pentacoordinate Si^V complex (**1H(1)RC-b**, eq 8). Formation of pentacoordinate silicon complexes in the condensed phase is well documented.[18] An analogous mechanism was observed and supported by calculations for the simple nucleophilic substitution reactions at silicon in the gas phase.[19] The HF/6-31G* geometries of the complex resulting from back attack, **1H(1)RC-b**, and of the transition state for the cleavage of the siloxane bond by front attack of water, **1H(1)TS-f**, are presented in Scheme 3.



(8)

The potential energy surface for this reaction is of the single-well type; that is, dissociation of the complex **1H(1)RC-b** to products proceeds without passing through any transition state. The course of the reaction was confirmed by PES calculations at the MP2/6-31G** level. The energy of the complex **1H(1)RC-b** relative to the substrates is −25.4 and −19.4 kcal/mol at MP4 and DFT, respectively (Table 1). The transition state **1H(1)TS-f** proposed by Xiao and Lasaga is ca. 22 kcal/mol higher in energy than the complex resulting from the back-side attack (Figure 1). Thus, the latter pathway seems to be preferable, although in the gas phase the front-side attack may also occur, as the energy of the transition state is approximately the same as the total energy of the substrates. Substitution with inversion of configuration at silicon is expected also on the basis of experimental data, as favored by two factors: the relative softness of the nucleophile (water) and the good leaving group (silanol).[18b]

Hydrolysis of the protonated siloxane **1H** by a water tetramer proceeds via the "early" complex, involving back-side attack of water, the transition state, and the "product" complex, whose structures resemble those for

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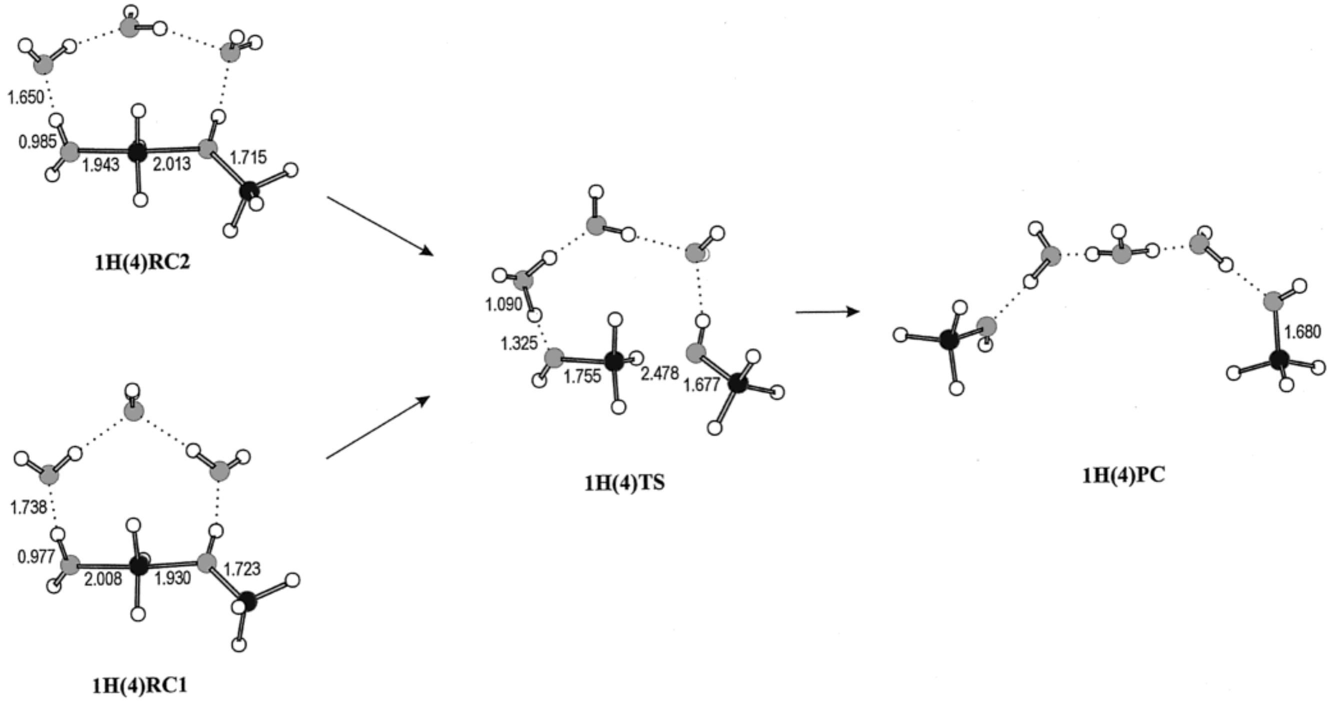
Scheme 4. Structures of the Reactive Complexes, 1H(4)RCn, Transition State, 1H(4)TS, and Product Complex, 1H(4)PC, for Hydrolysis of Protonated Disiloxane 1H by a Water Tetramer



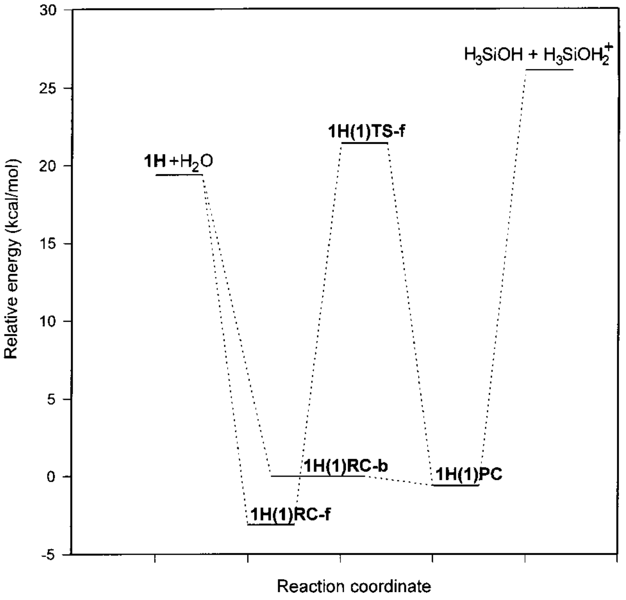


Figure 1. Energy (DFT) profiles for hydrolysis of protonated disiloxane **1H** via the back (**1H(1)RC-b**) and the front (**1H(1)RC-f**) attack of a water molecule.

the hydrolysis of **1** by $(H_2O)_4$. They are shown in Scheme 4. Two structures of the early complexes have been found; **1H(4)RC1** is ca. 1.5 kcal/mol more stable than **1H(4)RC2**, but both lead to the same transition state, **1H(4)TS**. The Si−O bond breaking is more advanced in **1H(4)TS** than in **1(4)TS** (compare Schemes 2 and 4). The energy barrier for the hydrolysis is 8.5 and 4.5 kcal/mol at MP4 and DFT levels, respectively (Table 1), 16−18 kcal/mol lower than that for the neutral hydrolysis. Thus, protonation of a siloxane by a protic acid dramatically reduces the activation energy of its hydrolysis by water clusters, in full agreement with kinetic observations[4,6,7] and with recent theoretical calculations.[5a,c] Comparison of the mechanism of hydrolysis of **1H** by a water monomer and a water tetramer points to the essential role of hydrogen-bonded aggregates in facilitating the hydrolysis. This observation fits very nicely the mechanistic scheme (Scheme 1) proposed by Chojnowski and Wilczek on the basis of kinetic data, according to which water trimers and tetramers are the active species responsible for proton transfer to the siloxane in acid-catalyzed siloxane bond cleavage.[8]

Cleavage of the Siloxane Bond in $H_3SiOSiH_2OH$ (2). Hydrolysis of the Si−OMe bond in $MeSi(OH)_2OMe$ by $(H_2O)_n$, $n = 1{-}4$, was studied by Yamabe et al.[5c] They found that the energy barrier at HF/6-31G* is lowered with increasing n, from 41 kcal/mol ($n = 1$) to 21 kcal/mol ($n = 4$). Only the front-side attack at silicon was considered. We performed calculations of the hydrolysis reaction of disiloxanol **2** by water clusters comprising up to four water molecules in neutral and acidic conditions (eq 9). The presence of a silanol group, capable of forming strong hydrogen bonds, gives rise to a variety of complexes with water of comparable energy, making it difficult to locate the stationary points on the reaction pathway. Nevertheless, hydrolysis of **2** by H_2O and $(H_2O)_2$ leads to reactive complexes and transition states similar to those found for the hydrolysis of $MeSi(OH)_2OMe$.[5c] The interaction with a single water molecule results in three reaction pathways **A**−**C** presented in Scheme 5.

$$H_3SiOSiH_2OH + (H_2O)_n \rightarrow H_3SiOH + H_2Si(OH)_2 + (H_2O)_{n-1} \quad (9)$$

Pathways **A** and **B** involve the rupture of the siloxane bond, whereas pathway **C** results in OH group ex-

Scheme 5. Structures of the Reactive Complexes, 2(1)RCn, Transition States, 2(1)TSn, and Product Complexes, 2(1)PCn, for Hydrolysis of Disiloxanol 2 by a Single Water Molecule

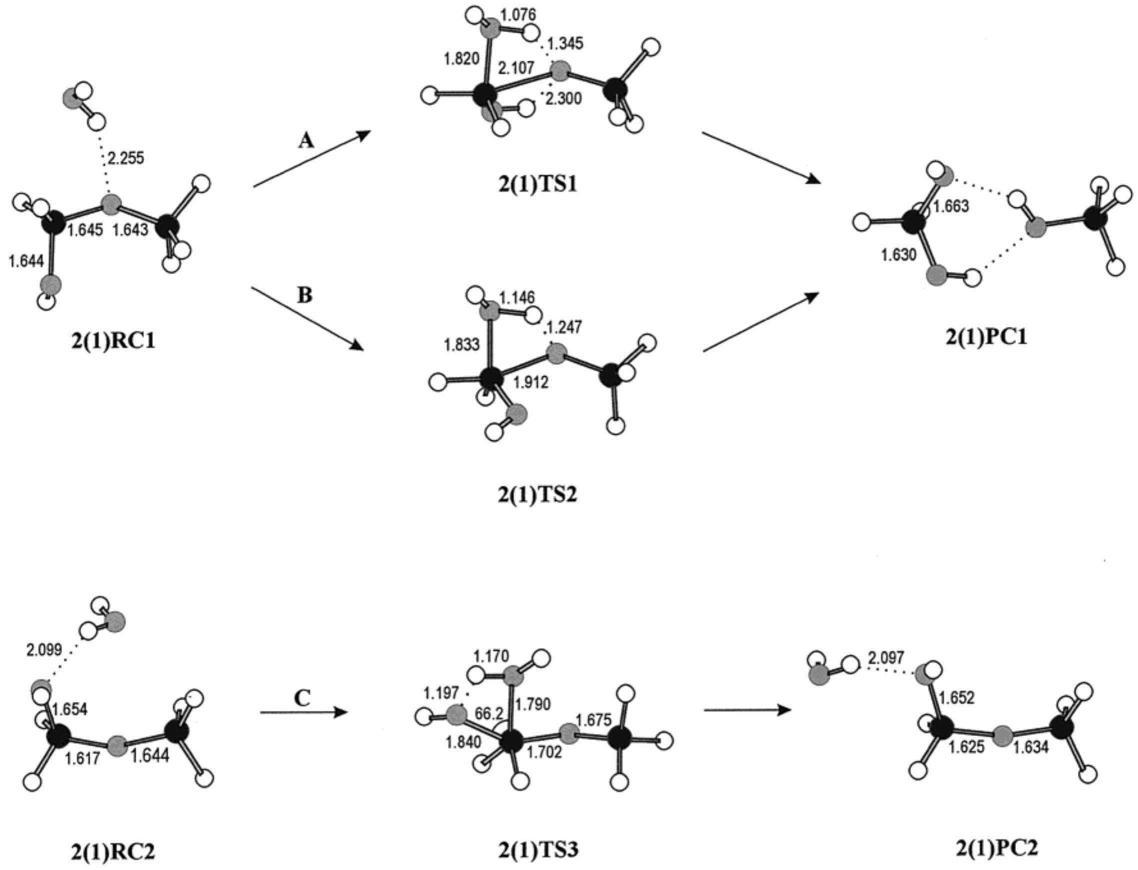


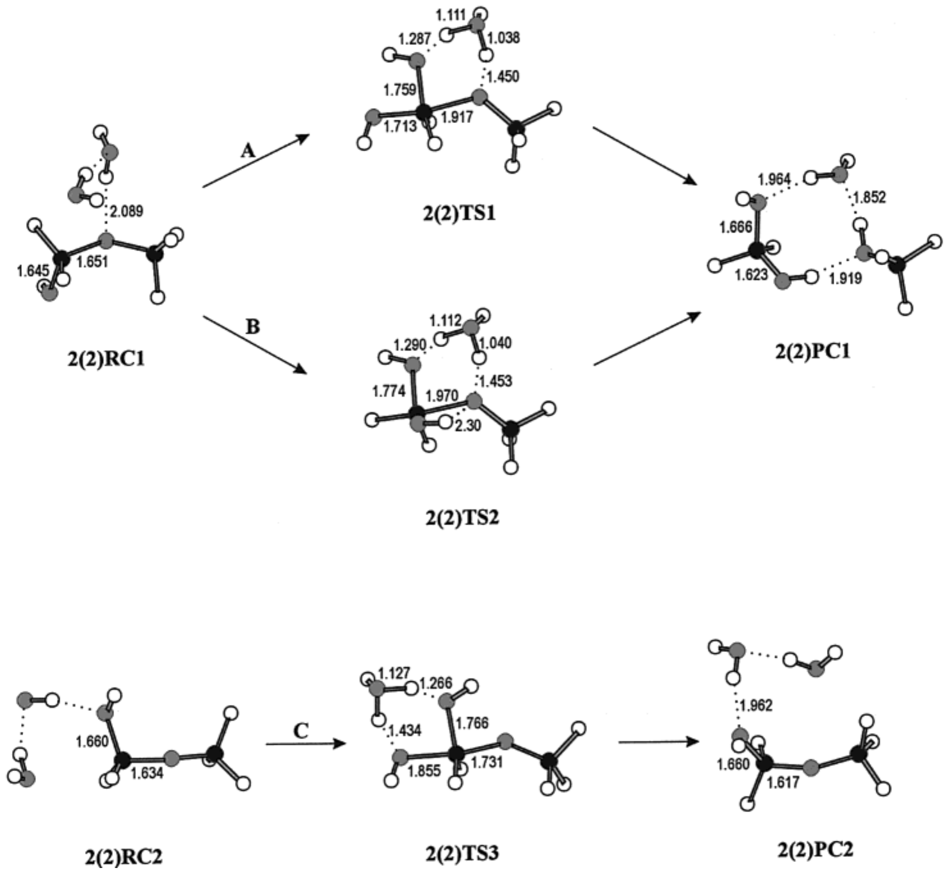
Table 2. Relative Energies (kcal/mol) for Hydrolysis of Disiloxanol (2) and Protonated Disiloxanol (2H) by Water Clusters $(H_2O)_n$, $n = 1, 2, 3, 4$

n	level[a]	substrates	RC (RC2)[b]	TS (TS2, TS3)	PC (PC2)	products
			2 + $(H_2O)_n \rightarrow H_3SiOH + H_2Si(OH)_2 + (H_2O)_{n-1}$			
1	HF	6.0	0	45.6 (44.1, 46.1)	2.7 (1.4)	
(Scheme 5)	MP4	9.1	0	32.1 (31.8, 34.2)	1.6 (2.7)	
	DFT	4.5	0	33.3 (31.9, 34.1)	0.0 (1.0)	
2	HF	11.7	0 (4.1)	43.6 (42.5, 39.9)	2.2 (3.1)	
(Scheme 6)	MP4	17.5	0 (6.5)	29.2 (29.1, 26.8)	1.8 (5.1)	
	DFT	6.5	0 (4.9)	29.2 (30.2, 26.6)	0.1 (4.0)	
3	HF		0	34.0 (35.1)	2.8	
(Scheme 7)	MP4		0	17.7 (18.3)	2.3	
	DFT		0	19.1 (20.0)	1.0	
4	HF		0	32.0	−5.7	
(Scheme 7)	MP4		0	13.5	−4.7	
	DFT		0	17.5	−8.2	
			2H + $(H_2O)_n \rightarrow H_3SiOH_2^{(+)} + H_2Si(OH)_2 + (H_2O)_{n-1}$			
1	HF	20.1	0	18.4	3.0	27.0
(Scheme 8)	MP4	24.5	0	21.6	3.8	32.0
	DFT	17.7	0	16.1	−1.6	23.9
2	HF	17.1	0	25.0	−2.2	
(Scheme 8)	MP4	20.8	0	27.8	−0.6	
	DFT	14.4	0	22.8	−4.4	
3	HF	26.4	0	16.9	−0.5	
(Scheme 8)	MP4	32.4	0	20.6	0.4	
	DFT	23.2	0	13.3	−4.9	
4	HF	32.9	0	6.4	−7.7	
(Scheme 9)	MP4	41.7	0	3.7	−6.5	
	DFT	31.1	0	−1.9	−11.0	

[a] HF = HF/6-31G*; MP4 = MP4/6-31G*//HF/6-31G*. DFT = B3LYP/6-311+G(2d,p)///HF/6-31G*. [b] In parentheses are given relative energies for additional structures RC2, PC2, TS2, and TS3; see Schemes 5−8.

change. Pathway **B** differs from **A** in the position of the OH group. In **A**, the SiOH group is positioned toward the leaving group, making the assistance in bond breaking possible, while in **B** it is turned in the opposite direction. The conformation **A** (**2(1)TS1**) is slightly lower in energy than **2(1)TS2** (by 0.1 and 1.6 kcal/mol

Scheme 6. Structures of the Reactive Complexes, 2(2)RCn, Transition States, 2(2)TSn, and Product Complexes, 2(2)PCn, for Hydrolysis of Disiloxanol 2 by a Water Dimer



at MP4 and DFT, respectively), indicating that the assistance of SiOH to the leaving group has little influence on the rate of the reaction, although the (silanol)H···O(siloxane) distance of 2.25 Å is well within the range of interaction. The OH group exchange (pathway **C**) requires about the same amount of energy as the siloxane bond cleavage **A** and **B**. The activation energy for the hydrolysis of **2** by monomeric water (32−33 kcal/mol at the MP4 and DFT levels) is almost identical to that for the hydrolysis of **1** (Tables 1 and 2), indicating that the presence of the geminal silanol group has little effect on the rate of hydrolysis of a siloxane bond by a water monomer.

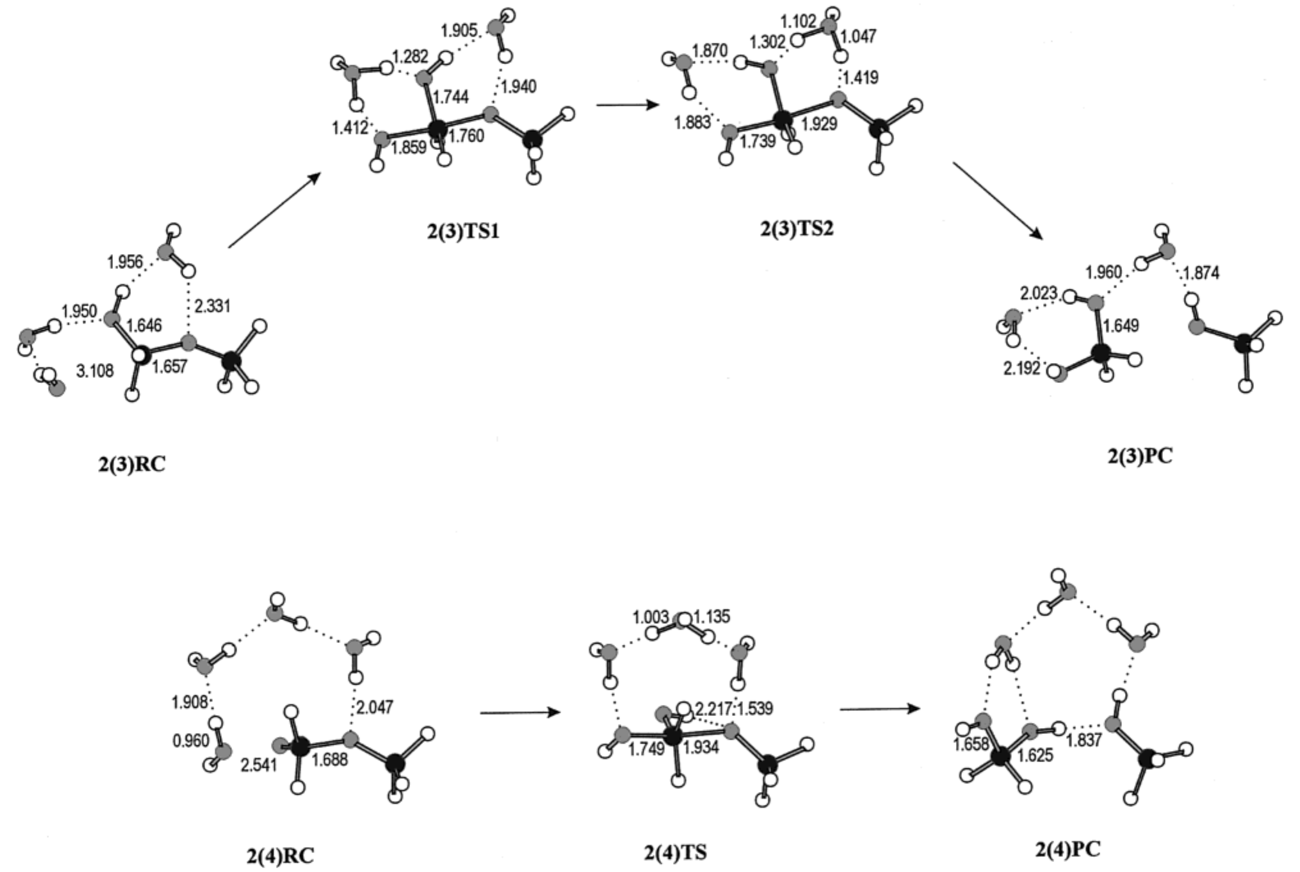
Hydrolysis of **2** by the water dimer proceeds as shown in Scheme 6. Both structures of the transition state have very similar energies; therefore the assistance of the SiOH group to the leaving group in this case is also of minor importance. The activation energy for the hydrolysis of **2** by $(H_2O)_2$ is 2−4 kcal/mol lower than that involving monomeric water. The HF/6-31G* energy barriers for the hydrolysis of **2** are 3−5 kcal/mol higher than those for the hydrolysis of methoxysilane.[5b] These results are in accord with experiment, as hydrolysis of the Si−OC bond in alkoxysilanes is faster than hydrolysis of the siloxane bond.[4c,g] The energy barrier for OH group exchange is 2−3 kcal/mol lower than cleavage of the siloxane bond.

In all cases the transition states are dominated by proton transfer from nucleophile to the leaving group. The search for the complex, in which the SiOH group would be involved in such transfer of proton, failed. This is due to the angular strain in such structures, when the water monomer or dimer is used. The SiOH group can participate in proton transfer when at least three molecules of water are engaged in the hydrolysis reaction (Scheme 7). Two transition states have been found in this case, having almost identical energies, one involving proton transfer from water acting as a nucleophile to the silanol oxygen, **2(3)TS1**, and the other transferring a proton to the siloxane oxygen, **2(3)TS2**. The latter is slightly higher in energy; therefore its relative energy is considered the overall barrier for hydrolysis ($E^{\ddagger} = 18.3$ and 20 kcal/mol at MP4 and DFT, respectively).

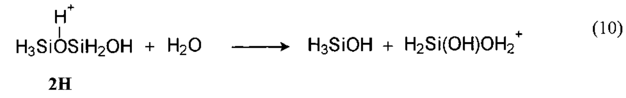
With four molecules of water, the structures of the reactive complex, **2(4)RC**, and the transition state, **2(4)TS**, are analogous to those found for the hydrolysis of **1** (Scheme 7). The MP4 and DFT barriers for hydrolysis are $\Delta E = 13.5$ and 17.5 kcal/mol, respectively. In this case, the SiOH group does not participate in proton transfer, but its position in the transition state structure indicates the possible interaction with the leaving group (the distance between the silanol hydrogen and the siloxane oxygen being 2.21 Å), which may be the reason for the lowering of the energy barrier. Thus, the rate of hydrolysis increases with increasing number of water molecules involved in the cluster, in agreement with previous studies,[5] and the participation of the SiOH group in the hydrogen bond complexes possibly facilitates the bond cleavage.

Acid hydrolysis of **2** was studied for the model reactions 10, 11, and 12. The geometries of the transi-

Scheme 7. Structures of the Reactive Complexes, Transition States, and Product Complexes for Hydrolysis of Disiloxanol 2 by Three and Four Water Molecules

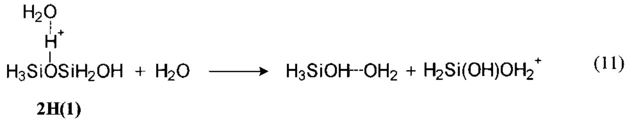


tion states are shown in Scheme 8, and their energies are shown in Table 2.



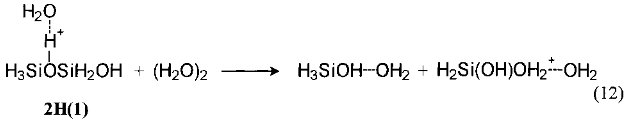
$$\mathrm{H_3Si\overset{\overset{H^+}{|}}{O}SiH_2OH + H_2O \longrightarrow H_3SiOH + H_2Si(OH)OH_2^+} \qquad (10)$$

2H



$$\mathrm{H_3Si\overset{\substack{H_2O\\ \vdots \\ H^+\\ |}}{O}SiH_2OH + H_2O \longrightarrow H_3SiOH{\cdots}OH_2 + H_2Si(OH)OH_2^+} \qquad (11)$$

2H(1)



$$\mathrm{H_3Si\overset{\substack{H_2O\\ \vdots \\ H^+\\ |}}{O}SiH_2OH + (H_2O)_2 \longrightarrow H_3SiOH{\cdots}OH_2 + H_2Si(OH)OH_2^+{\cdots}OH_2} \qquad (12)$$

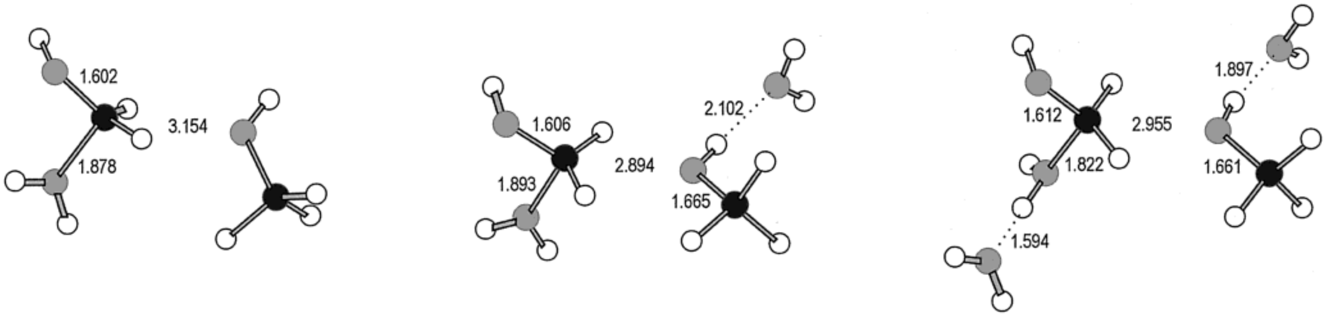
2H(1)

The activation energy for hydrolysis of **2H** by a single water molecule (eq 10, Scheme 8) is 21.6 and 16.1 kcal/mol at MP4 and DFT levels, respectively. These values are ca. 10 (MP4) and 15 (DFT) kcal/mol lower than the barrier for neutral hydrolysis. Coordination of a water molecule to the protonated siloxane bond increases the activation energy by ca. 6−7 kcal/mol (eq 11), because, due to the more efficient dispersion of the positive charge, the effect of protonation on the weakening of the siloxane bond is diminished. On the other hand, coordination of water to the nucleophile as in eq 12 lowers the energy barrier by about 8 kcal/mol, which confirms the importance of the base assistance responsible for the withdrawal of a proton from the nucleophile.

When a water tetramer was used for hydrolysis, a stable cyclic complex **2H(4)RC** is formed, in which a cooperative proton transfer from the nucleophile to the siloxane oxygen is possible (Scheme 9). This results in a dramatic drop of the activation energy to only 3.7 kcal/mol at the MP4 level (at DFT the energy of the TS is even negative, −1.9 kcal/mol, pointing to the inadequacy of the HF/6-31G* geometries for this model chemistry). The enthalpy and free energy of activation at the MP4 level are only 0.5 and 1.6 kcal/mol, respectively. Thus, hydrolysis of the protonated siloxanol by a water tetramer proceeds essentially with no energy barrier.

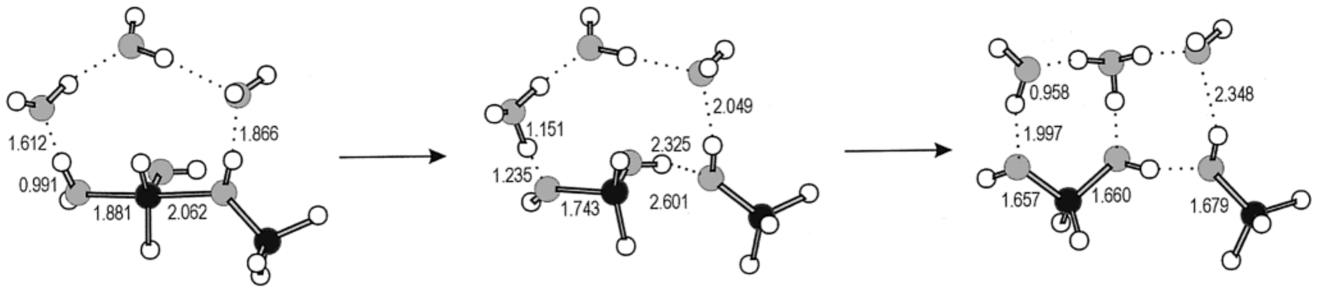
Basic Activation of the Nucleophile. Vibrational analysis of the various hydrolysis transition states shows that the motion along the reaction coordinate involves predominantly proton withdrawal from the nucleophile (a water or a silanol molecule) attacking the silicon. There is a considerable degree of dissociation of the leaving siloxy group in the TS. To examine the influence of a base assistance to the nucleophile, we have compared the energetics of hydrolysis of **2H(1)** by a water dimer (eq 12, Scheme 8) with that in which water complexed by dimethyl ether was used as a nucleophile (Scheme 10). Dimethyl ether was chosen as a model since it is more basic than water. Moreover, ethers (like dioxane) are commonly used, and they were shown to strongly affect the kinetics of silanol condensation.[4b,f] In the water-assisted reaction, a proton is not completely withdrawn from the H_2O molecule acting as a nucleophile. However, when the water molecule is replaced by dimethyl ether, the proton transfer from H_2O to ether in the transition state is much more advanced. This results in lowering of the energy barrier for the hydrolysis of **2H(1)** to 5.6 kcal/mol at HF/6-31G*

Scheme 8. Transition State Structures for Reactions 10, 11, and 12



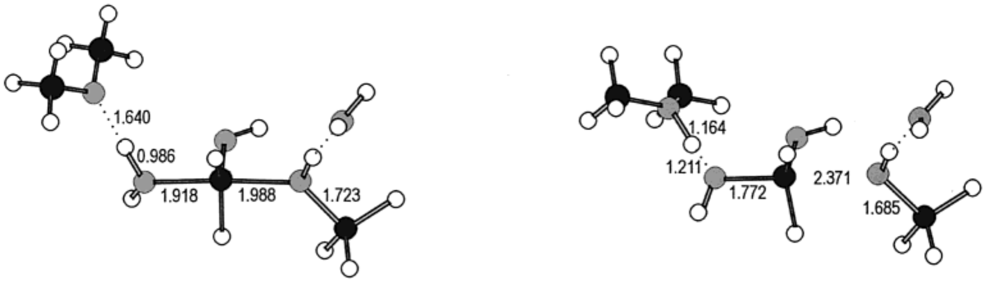
2H(1)TS **2H(2)TS** **2H(3)TS**

Scheme 9. Structures of the Reactive Complex, 2H(4)RC, Transition State, 2H(4)TS, and Product Complex, 2H(4)PC, for Hydrolysis of Protonated Disiloxanol 2H by a Water Tetramer



2H(4)RC **2H(4)TS** **2H(4)PC**

Scheme 10. Hydrolysis of 2H(1) by a Water−Dimethyl Ether Complex

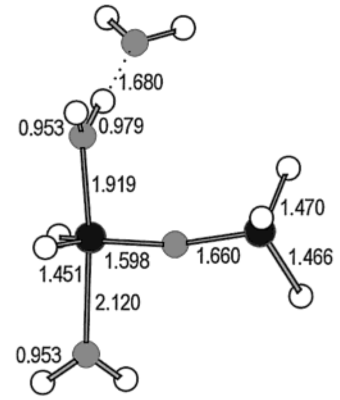


2H(2,Me$_2$O)RC **2H(2,Me$_2$O)TS**

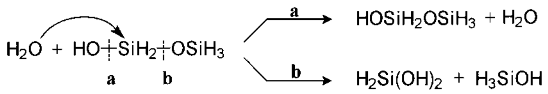
and to only 0.7 kcal/mol at DFT. The corresponding HF/6-31G* values of enthalpy and Gibbs free energy of activation for the reaction in the gas phase are $\Delta H^{\ddagger} =$ 2.4 kcal/mol, $\Delta G^{\ddagger} =$ 2.8 kcal/mol. Dimethyl ether, due to its higher basicity compared to water, reduces the activation barrier for the hydrolysis, being in fact a cocatalyst to the reaction.

In solution, the catalytic effect of acids on the hydrolysis of siloxanes is controlled by a subtle interplay between the acid strength and the basicity of the medium. If the basicity of the assisting species is small, it is unable to effectively withdraw the proton from the nucleophile and the hydrolysis reaction is slow. On the other hand, a base that is too strong neutralizes the acid, so that no protonation of the siloxane occurs, slowing down the hydrolysis, too. Ethers, water, alcohols, or other silanol molecules are capable of cocatalyzing the reaction. Siloxanes, being weak bases, are much less effective.[4b,8] Solvation plays an essential role in hydrolysis/condensation of siloxanols, affecting acid−base equilibria as well as structures of the reactive complexes and transition states. The reaction proceeds in hydrogen bond clusters, in which the local concentrations of reagents are very high. Therefore, the real rate constants may be very different from those estimated using classical kinetic laws regarding total concentrations of the reactive species in solution. This problem is often neglected, since the estimation of the effective concentrations of reagents in clusters is usually very difficult.[8]

Scheme 11. Transition State for the OH Group Exchange in Reaction of 2H with a Water Dimer



Competition between Silanol and Siloxane Bond Cleavage. Nucleophilic attack at silicon may result in substitution of the hydroxy (Si−OH) or the siloxy (Si−OSi) group. If the nucleophile is another silanol molecule, the former reaction leads to condensation, whereas the latter results in disproportionation of the siloxane oligomer. The contribution of disproportionation to the polycondensation process is determined by the relative activation energies of the two reactions. To estimate this contribution, we have calculated the reaction energetics for several model substitution reactions, using a water molecule as the nucleophile. In this case, the cleavage of the Si−OH bond leads to exchange of OH groups (eq 13, path **a**), while cleavage of the Si−OSi bridge produces silanol and silanediol (eq 13, path **b**).

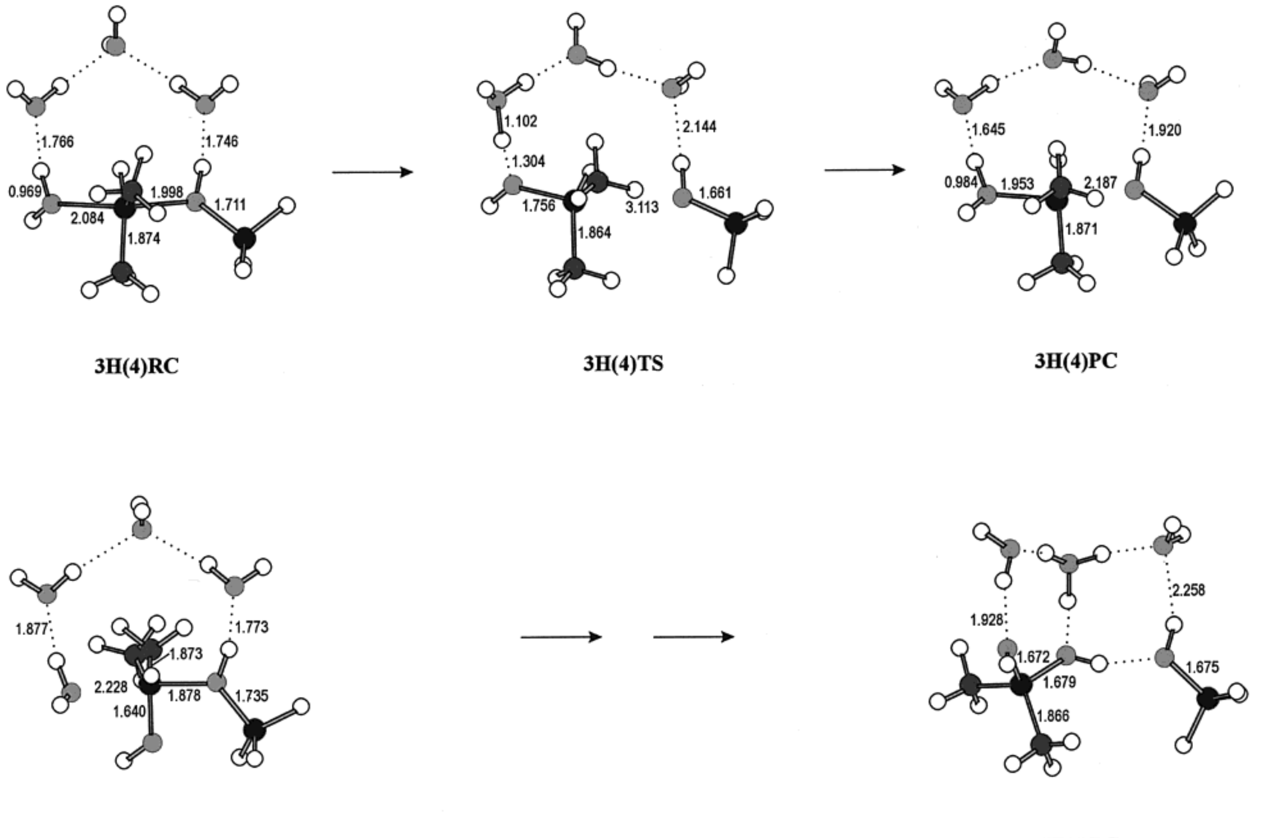


(13)

Under neutral conditions the barriers for the OH exchange are comparable with those of the siloxane bond splitting, for systems with one (Scheme 5) and two water molecules (Scheme 6). In acidic conditions, the exchange reaction becomes essentially barrierless (the calculated barriers are ca. 1 kcal/mol). The example of the structures of transition states is shown in Scheme 11. The ease of substitution of hydroxy group suggests strong preference of the condensation reaction over disproportionation. However, this preference is significantly reduced when hydrogen bond complexes such as **2H(4)RC** are involved in the Si−O bond cleavage.

Influence of Methyl Groups. Hydrogen-substituted siloxanes are very reactive and have little practical importance. However, they are the models of choice for the theoretical calculations. To verify, whether the theoretical conclusions presented here are valid for the practically important methyl-substituted siloxanes, calculations of hydrolysis by a water tetramer were repeated for the model siloxanes having methyl groups at silicon, i.e., $H_3SiO(H^+)SiMe_2H$ (**3H**) and $H_3SiO(H^+)SiMe_2OH$ (**4H**). The equilibrium geometries of the reactive complexes, transition states, and product intermediates are analogous to those for hydrogen siloxanes **1** and **2**, respectively (Scheme 12). The activation energy for the hydrolysis of **3H** is 6.5 (HF), 7.3 (MP4), and 1.0 (DFT) kcal/mol. These values are consistent with those obtained for the reaction **1H** + $(H_2O)_4$ (Table 1).

Scheme 12. Structures of the Reactive Complexes, Transition State, and Product Complexes for Hydrolysis of Protonated Dimethyldisiloxane, 3H, and Dimethyldisiloxanol, 4H, by a Water Tetramer



3H(4)RC **3H(4)TS** **3H(4)PC**

4H(4)RC **4H(4)PC**

Attempts to find the geometry of the transition state for the hydrolysis of **4H** failed. Optimization starting from the geometry of the reactive complex, **4H(4)RC**, modified by shifting the proton of the attacking water molecule toward the assisting water molecule led to the structures of product complexes in which the siloxane bond cleavage was well advanced. Since the structures of the reactive complex (RC) and the product complex (PC) are very similar to those for the complexes involving fully hydrogen-substituted species, **2H(4)RC** and **2H(4)PC** (compare Schemes 9 and 12), the reaction pathway is likely to be also closely analogous. The difficulties with finding the transition state geometry are due to the fact that the potential energy surface for this process is very flat.

Thus, we conclude that substitution of the hydrogens at silicon by methyl groups does not affect significantly the rate of hydrolysis of siloxanes.

Solvent Effects. The changes in the calculated activation energy for the cleavage of the siloxane bond, depending on the hydrogen bond association of the siloxane with water or dimethyl ether, indicate the role of solvation in hydrolysis of siloxanes. To mimic more closely the experiment, some of the reactive complexes and transition states were recalculated using the polarized continuum method (SCRF PCM[14]) assuming dichloromethane as a solvent. Dichloromethane has often been used as a solvent for kinetic studies, since it is inert toward acids and bases, shows a little tendency to form hydrogen bonds, and is moderately polar (dielectric constant $\epsilon = 8.9$).[4] The results of the SCRF PCM calculations are presented in the Supporting Information.

For the neutral species we find that the energy barriers do not change much on going from the gas phase to methylene chloride. In contrast, for hydrolysis of the protonated species the energy barriers significantly decrease in CH_2Cl_2, indicating better stabilization of the charged transition states in solution relative to the gas phase. The activation energy for the hydrolysis of **2H** with $(H_2O)_4$ in CH_2Cl_2 is very close to zero, indicating that in such hydrogen bond clusters the siloxane bond cleavage is predicted to proceed very smoothly. The SCRF models are very crude approximations to solvent effects, and in principle, they can only estimate the electrostatic part of solvation forces. However, the hydrogen bond complex with several molecules of water may be treated roughly as the reaction center inside the first solvation shell. It seems reasonable to assume that the calculated energy barrier for the reaction should change asymptotically to the true value with an increasing number of molecules in the complex, as the model approaches real situation in solution. There should be the minimal number of molecules (solvent, H_2O) in the complex, exceeding which the further change in energy barrier would be insignificant. Since the energy barrier for hydrolysis with a water tetramer in acidic conditions is close to zero, the minimal number fulfilling the above condition is 4, in agreement with kinetic results.[8]

Conclusions

The hydrolysis of the siloxane bond in disiloxane and disiloxanol was studied theoretically, both in the neutral and in the protonated molecules, modeling neutral and acidic conditions. The effect of the following factors on the rate of the cleavage of the siloxane bond was determined: the participation of a proton, or a hydronium ion, and of the hydrogen bond complexes in the reaction center; the effect of a OH group geminal to the reactive siloxane bond.

We find that protonation dramatically reduces the energy barriers of the cleavage reaction, being the most important factor determining the rate of this process. The other important factor reducing the energy barrier of the siloxane bond cleavage is the participation of hydrogen-bonded water complexes, which effectively contribute to the transfer of a proton from the nucleophile to the leaving group. The water cluster−siloxane hydrogen bond complexes play an important role in the condensed phase, and some of a large variety of possible structures are presented here. These complexes may consist of water, silanol, and acid. The energy barrier for siloxane bond cleavage decreases as the number of water molecules in the hydrogen bonded water cluster increases.

SCRF calculations indicate that the energy barriers for neutral hydrolysis do not change much compared to those in the gas phase, but the barriers for hydrolysis of the protonated species significantly decrease, due to better stabilization of the charged transition states. The activation energy for acid-catalyzed hydrolysis of disiloxanol by the water tetramer in solution is virtually barrierless.

The reasons for the experimentally observed enhanced reactivity of the terminal silanol unit in siloxanols are not fully understood. It is partly due to the ability of the SiOH group to participate in hydrogen-bonded structures, responsible for proton transfer to the siloxane oxygen, and also to provide assistance to the leaving group, making the bond breaking easier. The asymmetry of the hyperconjugative and inductive effects at the siloxane chain end may be the other reason for this behavior. It should also depend on the proton donating/accepting ability of the solvent. Further explanation is a subject of the separate study.

Acknowledgment. M.C. is indebted to Professor Julian Chojnowski, whose contribution to the understanding of the role of hydrogen bond complexes in the siloxane bond formation was an inspiration to this work. M.C. also thanks the Polish and Israeli Academies of Sciences for the travel grant.

Supporting Information Available: The Cartesian coordinates of all the species considered in this work and the results of SCRF calculations are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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