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Hydrolysis of Fluorosilanes: A Theoretical Study

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Hydrolysis and condensation of simple trifluorosilanes, $HSiF_3$ and $MeSiF_3$, was studied by quantum mechanical methods. Hydrolysis of fluorosilanes is highly endothermic. The Gibbs free energy of the first reaction step in the gas phase is 31.4 kJ/mol, which corresponds to an equilibrium constant of 10^{-6}. Hydrolysis of the subsequent fluorine atoms in trifluorosilanes is thermodynamically more unfavorable than the first step of substitution. No significant difference in thermodynamics of hydrolysis was found between $HSiF_3$ and $MeSiF_3$. The activation energy for hydrolysis by a water dimer is significantly lower than that for hydrolysis by a water monomer. The former reaction is also less unfavorable thermodynamically, due to a high binding energy of the $HF{-}H_2O$ complex formed as a product of hydrolysis. Self-consistent reaction field (SCRF) calculations show that hydrolysis of trifluorosilanes in aqueous medium has lower activation energy than in the gas phase. It is also thermodynamically less unfavorable, due to better solvation of the products. Homofunctional condensation of $HSiF_2OH$ is thermodynamically favored. The equilibrium mixture for hydrolysis/condensation of $RSiF_3$ in water is predicted to contain ca. 2.3% disiloxane $(HF_2Si)_2O$, if 100-fold excess of water relative to silane is assumed. Further hydrolysis of $(HF_2Si)_2O$ is negligible. The thermodynamics of fluorosilane hydrolysis contrasts with that of chlorosilanes, where both hydrolysis and condensation are strongly favorable. Moreover, in the case of trichlorosilanes each subsequent hydrolysis step is more facile, leading to the product of full hydrolysis, $RSi(OH)_3$.

Introduction

Fluorosilanes are useful materials in plasma chemical vapor deposition processes (CVD), in the semiconductor industry, and in optical fiber production.[1−3] They find application for the synthesis of highly coordinated silicon compounds[4] and highly hindered organosilanes.[5] Recently, they have also been suggested to be useful as precursors to polysilsesquioxanes and fluorosilsesquioxanes.[6,7]

Therefore, the reactivity of the Si−F function is of increasing interest for both experimental and theoretical chemists.[8−11] Here we present the results of quantum chemical calculations on thermodynamic and kinetic aspects of hydrolysis of trifluorosilanes, mostly from the point of view of their potential application in silsesquioxane synthesis.

The Si−F bond is one of the strongest known in chemistry. Its energy is as high as 638−697 kJ/mol compared to 512−570 kJ/mol for the Si−O bond.[12] Fluorosilanes are therefore very stable, although strong polarization of the bond makes it under certain conditions susceptible to heterolytic cleavage.

Thermodynamic data concerning fluorosilanes are very scarce. To our knowledge, there is no experimental data on thermodynamics of fluorosilane hydrolysis. Measurements of thermodynamic quantities for this process may give different results depending on reaction conditions, as the energetics of hydrolysis is strongly affected by association phenomena.

It is reasonable to compare thermodynamics of hydrolysis of fluorosilanes with that of chlorosilanes, which has been studied much more extensively. The enthalpy of hydrolysis of trimethylchlorosilane (reaction 1) in the gas phase, deduced from bond dissociation enthalpies (BDEs) for all bonds involved, is −4.2 kJ/mol. (BDEs for silicon compounds were taken from ref 13; BDEs for H_2O and HCl were taken from ref 14.) In acidic conditions it is difficult to stop the reaction at the stage of silanol, because hydrolysis is accompanied by rapid condensation of silanol leading to siloxane. Therefore, it is more appropriate to compare the total enthalpies of hydrolysis and condensation (reaction 2). The enthalpy of this reaction, deduced analogously from BDEs, is ca. −21 kJ/mol in the gas phase. The studies on hydrolytic condensation in the gas phase have shown incomplete conversion of alkylchlorosilanes in excess of water, due to the reversibility of the reaction:[15]

$$Me_3SiCl + H_2O \rightarrow Me_3SiOH + HCl \qquad (1)$$

$$2Me_3SiCl + H_2O \rightarrow (Me_3Si)_2O + 2HCl \qquad (2)$$

The enthalpy of reaction 2 for aqueous hydrolysis was measured to be as large as −46 to −52 kJ/mol.[16] A considerable contribution to the heat produced in hydrolysis comes from the heat of HCl hydration. Independently reported free energy value of −74 kJ/mol for the aqueous hydrolysis of Me_3SiCl at constant volume conditions corresponds to an equilibrium constant of 9.5×10^{12}.[17] These data show that the thermodynamics is very favorable for this process and should proceed to virtually full conversion of chlorosilane. However, it was shown that some amount of SiCl may remain unhydrolyzed when saturated aqueous HCl is in equilibrium with the final hydrolysis products, due to the fact that the thermodynamic activity coefficient for HCl in concentrated HCl solution is very high, while that for H_2O is low.[18] Thus, the overall energy and equilibrium position

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of this process strongly depends on the water/silane proportion and on the polarity of the medium and its ability to hydrogen-bond.

The enthalpies of analogous reactions of Me_3SiF in the gas phase, deduced from BDEs, are 29 and 46 kJ/mol for reactions 3 and 4, respectively. Thus, in contrast to chlorosilanes, hydrolysis of fluorosilanes is thermodynamically unfavorable. This is, of course, what was expected, since the stronger Si−F bond is replaced in this process by the weaker Si−O bond. These estimations have been supported by DFT calculations. The B3LYP/6-311G(2d,2p) calculated enthalpy for hydrolysis of SiF_4 is 37.6 kJ/mol (reaction 5). Gibbs free energy for this reaction was 65.3 kJ/mol, which corresponds to an equilibrium constant K in the range of 10^{-12}−10^{-11}:[10]

$$Me_3SiF + H_2O \rightarrow Me_3SiOH + HF \quad (3)$$

$$2Me_3SiF + H_2O \rightarrow (Me_3Si)_2O + 2HF \quad (4)$$

$$2SiF_4 + H_2O \rightarrow (F_3Si)_2O + 2HF \quad (5)$$

According to this result, hydrolysis of SiF_4 in the gas phase practically does not occur. However, to our knowledge, there is no experimental data on thermodynamics of fluorosilane hydrolysis in solution. In aqueous medium HF forms strong associates (self-aggregates and hydrates) what may shift the equilibrium toward the products. Indeed, in the reaction of 2,6-$Mes_2C_6H_3SiF_3$ in water/THF, the amount of disiloxane $(Mes_2C_6H_3SiF_2)_2O$ was reported to reach ca. 3%.[6] Thus, to shed more light on thermodynamics of this reaction was the primary aim of this study.

Theoretical Methods

All calculations were performed with the Gaussian 03 program.[19] Equilibrium geometries were optimized with the HF/6-31+G(d) method. All stationary points, ground and transition states, were verified by frequency analysis. Thermal corrections to enthalpy and entropy at 298 K were scaled by 0.893. Final electronic energies were calculated at the B3LYP/6-311+G-(2d,p) level. This method will be denoted as DFT1 hereafter. In most cases, geometries of model species were further refined by use of Becke's three-parameter hybrid density functional B3LYP[20] and Pople's 6-31+G(d,p) basis set.[21] Comparison of the B3LYP/6-311+G(2d,p)//HF/6-31+G(d) (DFT1) and B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p) energies of complex formation and of reaction barriers shows that there is virtually no difference between these two methods. That means that the computational errors fortuitously cancel out for the most part. Some reaction systems were also calculated by very accurate compound G3B3[22] and CBS-QB3[23] methods. In most cases, no significant difference was observed for reaction energies computed with these methods. Thus, we might assume that the DFT1 method we used is accurate enough for this particular problem. Reliability of the calculation method was also confirmed by comparison of the geometries of model compounds with experimentally determined structures (see below). BSSE corrections were calculated by the method of Boys and Bernardi[24] and the counterpoise option in Gaussian. Self-consistent reaction field method (SCRF/DFT1), with the polarizable continuum model (PCM) using the integral equation formalism model (IEF) developed by Tomasi and co-workers (IEF−PCM) and atomic radii optimized for the HF/6-31G(d) level of theory (UAHF united atom topological model) was applied to estimate the solvent effect in water.[25]

Results

Simple trifluorosilanes, $HSiF_3$ and $MeSiF_3$, were used as model compounds. Energies of reaction and energy barriers were calculated for three hydrolysis steps (reactions 6−8), where R = H, Me:

$$RSiF_3 + H_2O \rightleftharpoons RSiF_2OH + HF \quad (6)$$

$$RSiF_2OH + H_2O \rightleftharpoons RSiF(OH)_2 + HF \quad (7)$$

$$RSiF(OH)_2 + H_2O \rightleftharpoons RSi(OH)_3 + HF \quad (8)$$

There are several interesting points on which we tried to focus: first, how the energy changes from one step to another, that is, how the presence of OH group(s) at silicon affects the thermodynamics and the rate of hydrolysis; second, how thermodynamic parameters are affected by an increasing number of water molecules participating in hydrolysis; third, what is the influence of HF on energetics of hydrolysis (since hydrolysis of silanes is catalyzed by acids, we might expect an autocatalytic effect by HF); and fourth, how a polar solvent (water) affects the thermodynamics and kinetics of the reaction (within the SCRF approximation). On the other hand, it is particularly interesting to compare these results with the hydrolysis of chlorosilanes.

Thus, we compared the reaction energies ΔE, Gibbs free energies ΔG, and the reaction barriers $\Delta E^{\ddagger}$ for each step of hydrolysis, and the results for each point of interest are presented below.

Geometries. Calculated geometries of model compounds agree well with those reported from experiment. Thus, the bonding parameters for $HSiF_3$, r(SiF) = 1.574 Å, r(SiH) = 1.446 Å, and ∠FSiF = 108.0°, correspond to those obtained from microwave spectroscopy (1.565 Å, 1.455 Å and 108.2°, respectively).[26] For $MeSiF_3$, the corresponding parameters are r(SiF) = 1.579 (1.570) Å, r(SiC) = 1.843 (1.836) Å, and ∠FSiF = 106.9° (106.8°), where experimental values determined by electron diffraction are given in parentheses.[27] Similar agreement was found between experimental and DFT1 calculated geometries of $HSiCl_3$. The bond distances and angles in $HSiCl_3$, r(SiCl) = 2.038 (2.020) Å, r(SiH) = 1.464 (1.453) Å, ∠ClSiCl = 109.4° (109.6°), and ∠HSiCl = 109.5° (109.4°), agree well with the microwave spectroscopic values given in parentheses.[28] Generally, bond angles are in excellent agreement with experiment, while bond distances are in most cases slightly too long, as a result of using a basis set with diffuse functions.

Influence of OH Substituents on the Energy of Hydrolysis. Calculated geometries of the reactive complexes and transition states are shown in Figures 1 and 2. They are analogous to the corresponding structures found in hydrolysis of trichlorosilanes, proving that the mechanism of both processes is the same.[29−31] Electronic energies, Gibbs free energies, and reaction barriers of each step of hydrolysis in the gas phase are presented in Table 1. The reaction pathway consists of the following stationary points, geometries and energies of which were calculated:

$$\underset{\text{(free substrates)}}{RSiF_3 + H_2O} \rightleftharpoons \underset{\text{(reactive complex, RC1)}}{RSiF_3\cdots H_2O} \rightleftharpoons \underset{\text{(transition state, TS)}}{[RSiF_3\cdots H_2O]^{\ddagger}} \rightleftharpoons \underset{\text{(late reactive complex, RC2)}}{RSiF_2OH\cdots HF} \rightleftharpoons \underset{\text{(free products)}}{RSiF_2OH + HF} \quad (9)$$

TABLE 1: Relative Energies and Gibbs Free Energies for the Stepwise Hydrolysis of $HSiF_3$ and $MeSiF_3$[a]

method[b]	RC1 (BSSE)[c]	TS	RC2 (BSSE)	products (ΔG^{298})[d]	K^e
$HSiF_3 + H_2O \rightarrow HSiF_2OH + HF$					
DFT1	−16.7 (−12.6)	107.1	8.0 (10.5)	33.5 (29.3)	2.7×10^{-6}
DFT2	−16.7 (−12.6)	106.3	8.0 (10.5)	33.9 (33.5)	
CBS-QB3	−12.1	109.2	18.8	33.1 (31.8)	
G3B3	−12.1	110.5	15.1	32.6 (31.8)	
$HSiF_2OH + H_2O \rightarrow HSiF(OH)_2 + HF$					
DFT1	−11.7 (−8.4)	97.9	3.8	40.0 (39.8)	9.1×10^{-8}
DFT2	−11.3 (−8.0)	97.9	3.8	40.6 (41.0)	
CBS-QB3	−22.6	105.9		38.9 (41.0)	
G3B3	−22.2	103.8		38.5 (40.0)	
$HSiF(OH)_2 + H_2O \rightarrow HSiF(OH)_2 + HF$					
DFT1	−27.2	110.5	3.8	44.8 (44.4)	2.8×10^{-8}
DFT2	−28.5	108.4		45.2 (45.6)	
CBS-QB3				41.9 (44.4)	
G3B3				41.4 (43.1)	
$MeSiF_3 + H_2O \rightarrow MeSiF_2OH + HF$					
DFT1	−14.2 (−10.9)	114.3	6.3	36.8 (35.6)	3.5×10^{-7}
DFT2	−14.2 (−10.9)	114.3	5.9	36.8 (36.4)	
G3B3				35.2 (36.8)	
$MeSiF_2OH + H_2O \rightarrow MeSiF(OH)_2 + HF$					
DFT1	−30.1	104.6	5.9	48.1 (47.3)	9×10^{-9}
DFT2				48.1 (47.7)	
G3B3				43.9 (46.0)	
$MeSiF(OH)_2 + H_2O \rightarrow MeSiF(OH)_2 + HF$					
DFT1	−36.0	109.6	1.7	50.6 (49.8)	3.3×10^{-8}
DFT2				45.6 (45.6)	
G3B3				42.3 (42.7)	

[a] Relative energies (0 K) and Gibbs free energies (298 K) are given in kilojoules per mole. All substrate energies were set at 0.0 kJ/mol. [b] DFT1 = B3LYP/6-311+G(2d,p)//HF/6-31+G(d); DFT2 = B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p). [c] BSSE-corrected values are given in parentheses; no correction for CBS-QB3 and G3B3. [d] ΔG^{298} values are given in parentheses. [e] Equilibrium constant $K = e^{-\Delta G/RT}$ for ΔG^{298} calculated at G3B3.

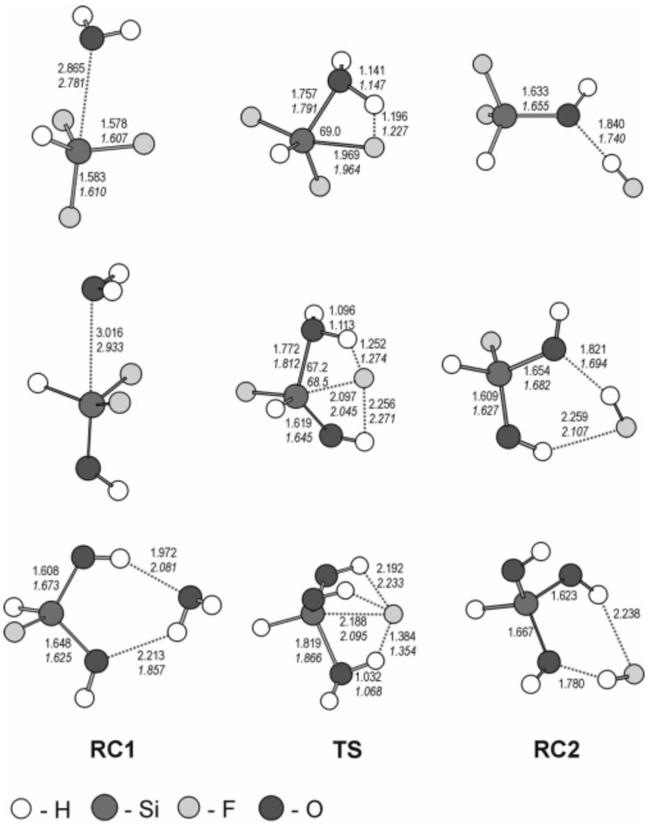

Figure 1. HF/6-31+G* optimized structures of RC1 and RC2 reactive complexes and transition states for hydrolysis of $HSiF_3$. Bond lengths are given in angstroms, angles are given in degrees, and B3LYP/6-31+G** bonding parameters are shown in italic type.

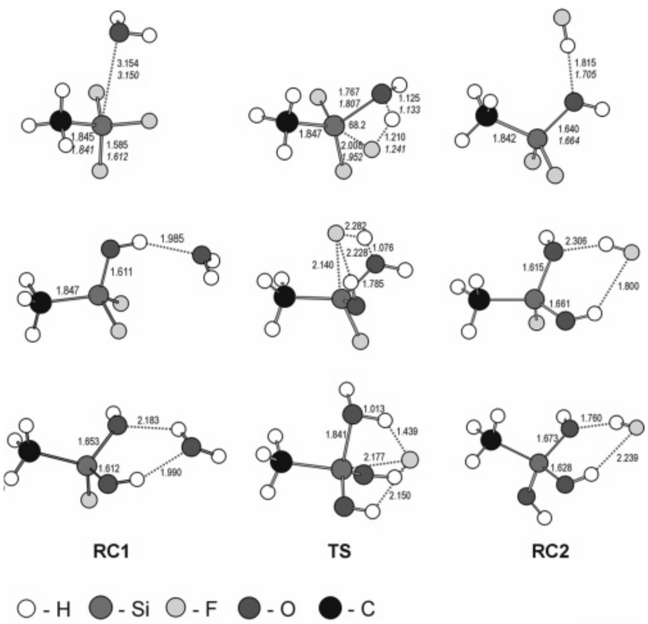

Figure 2. HF/6-31+G* optimized structures of RC1 and RC2 reactive complexes and transition states for hydrolysis of $MeSiF_3$. Bond lengths are given in angstroms, angles are given in degrees, and B3LYP/6-31+G** bonding parameters are shown in italic type.

Gibbs free energies of reaction were calculated as differences between the sums of energies of the free products and free substrates. Energy barriers were defined as differences between the energies of the transition state and of the sum of free substrates.

The relative energy values obtained by various methods are very close to each other. Thus, we may conclude that the simplest DFT1 method (i.e., B3LYP/6-311+G(2d,p)//HF/6-31+G*) provides results of a sufficient accuracy. DFT1 energies (33.5−42 kJ/mol) and energy barriers (100−109 kJ/mol) are in good agreement with those obtained for the hydrolysis of SiF_4 to SiF_3OH at the B3LYP/6-311G(2d,2p) level of theory ($\Delta E = 35$, $\Delta E^{\ddagger} = 96.4$ kJ/mol).[10] The barriers for hydrolysis

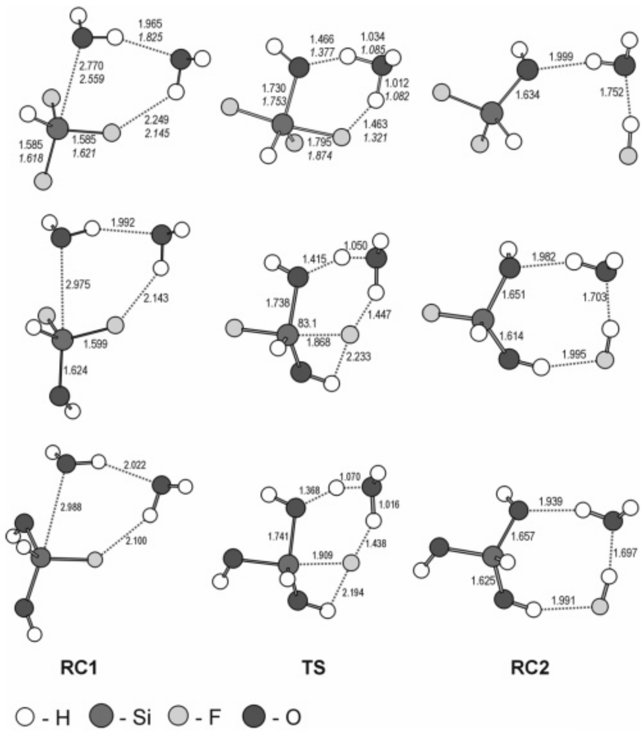

Figure 3. HF/6-31+G* optimized structures of reactive complexes and transition states for hydrolysis of $HSiF_3$ by $(H_2O)_2$ and HF−H_2O. Bond lengths are given in angstroms, angles are given in degrees, and B3LYP/6-31+G** bonding parameters are shown in italic type.

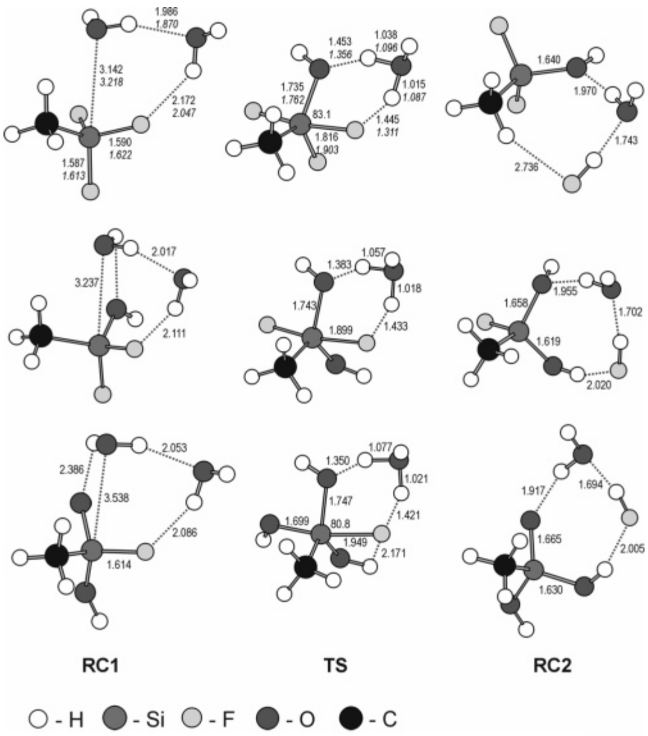

Figure 4. HF/6-31+G* optimized structures of reactive complexes and transition states for hydrolysis of $MeSiF_3$ by $(H_2O)_2$. Bond lengths are given in angstroms, angles are given in degrees, and B3LYP/6-31+G** bonding parameters are shown in italic type.

of fluorosilanes are considerably higher than those for chlorosilanes. Hydrolysis of fluorosilanes is therefore predicted to be considerably slower. Moreover, the barriers for consecutive hydrolysis steps are very similar, indicating that the effect of OH group assistance on the rate of hydrolysis of fluorosilanes is insignificant. This contrasts with the reactivity of chlorosilanes, where the energy barriers strongly decrease with increasing number of OH groups at silicon.[29−31] This difference can be explained by higher polarizability of Si−Cl bonds compared to Si−F, resulting in greater sensitivity of the chlorine leaving groups to electrophilic assistance.

In contrast to chlorosilanes, hydrolysis of the Si−F bond is highly endothermic. Gibbs free energy for $HSiF_3$ is above 31 kJ/mol, which corresponds to an equilibrium constant of 2.7×10^{-6}. ΔG increases slightly with increasing number of OH groups at silicon, indicating that further hydrolysis is even more unfavorable than the first step.

There is no significant difference in energetics between hydrolysis of $HSiF_3$ and of $MeSiF_3$. The corresponding free energies and energy barriers for $MeSiF_3$ are higher by ca. 4 kJ/mol, which probably reflects the steric hindrance of the methyl group.

Influence of Larger Water Complexes, $(H_2O)_2$ and HF−H_2O. Hydrolysis by a single water molecule can occur only in the gas phase. In condensed phases, larger hydrogen-bonded clusters are typically involved. Therefore, the energetics of hydrolysis by water dimer and by higher associates is of interest. It is known that the energy barrier for hydrolysis of chlorosilanes decreases with increasing number of water molecules participating in the reaction down to negligible values.[29,30] Similar behavior was also observed in the case of hydrolysis of siloxanes.[32] This is due to the released strain in the transition state, compared to simple bimolecular hydrolysis (compare Figure 1 with Figure 3 and Figure 2 with Figure 4). Moreover, the cooperativity of hydrogen bonds in the cyclic transition state facilitates proton transfer from water molecule acting as a nucleophile to the leaving group (chloride or silanolate anion), by a better stabilization of charge. The same trend is observed for fluorosilanes (reaction 10). Energy barriers for hydrolysis by water dimer are lower by 37−58 kJ/mol than the corresponding barriers for hydrolysis by a single water molecule (Table 2). The difference in reaction barriers between $HSiF_3$ and $MeSiF_3$ is 12−17 kJ/mol, which suggests that the steric effect is here more important than in hydrolysis by a water monomer. While the barrier heights for the latter reaction are determined by a strain in the four-membered cyclic transition state, the geometries of transition states for hydrolysis by water dimer are practically unstrained. Thus, the effect of steric hindrance at silicon may become more significant.

$$RSiF_3 + (H_2O)_2 \rightleftharpoons RSiF_2OH + HF{-}H_2O \qquad (10)$$

$$RSiF_3 + HF{-}H_2O \rightleftharpoons RSiF_2OH + (HF)_2 \qquad (11)$$

The equilibrium constants deduced from Gibbs free energies of the reaction with water dimer are higher than in the case of reactions 6−8, indicating that hydrolysis is more advanced in this case. This energy gain is due to higher binding energy in the HF−H_2O complex compared to water dimer.

We examined also the $HSiF_3$−$(H_2O)_2$ complex of tetragonal bipyramidal geometry with central hexacoordinate silicon atom and water molecules located in axial positions. Such a structure was considered by Corriu and Guérin[33] as an intermediate in nucleophile-catalyzed hydrolysis of halosilanes and was recently a subject of a theoretical study.[34] However, this complex is higher in energy by 96.5 kJ/mol than the RC1 complex shown in Figure 3, and therefore its participation in hydrolysis is highly improbable.

Hydrolysis by the HF−water complex (reaction 11) is faster than hydrolysis by water monomer but not as fast as the reaction

TABLE 2: Relative Energies and Gibbs Free Energies for the Stepwise Hydrolysis of $HSiF_3$ and $MeSiF_3$ by $(H_2O)_2$ and $HF-H_2O$[a]

method[b]	RC1 (BSSE)[c]	TS	RC2 (BSSE)	products (ΔG^{298})[d]	K[e]
		$HSiF_3 + (H_2O)_2 \rightarrow HSiF_2OH + HF-H_2O$			
DFT1	−27.6 (−22.6)	46.5	−4.2	15.2 (14.6)	2.7×10^{-3}
G3B3				12.6 (13.4)	4.5×10^{-3}
		$HSiF_2OH + (H_2O)_2 \rightarrow HSiF(OH)_2 + HF-H_2O$			
DFT1	−23.9 (−19.7)	51.1	−19.3	23.0 (25.1)	4×10^{-5}
G3B3				18.0 (22.2)	1.3×10^{-4}
		$HSiF(OH)_2 + (H_2O)_2 \rightarrow HSi(OH)_3 + HF-H_2O$			
DFT1	−18.4 (−14.6)	61.9	−22.2	27.6 (30.1)	5.3×10^{-6}
G3B3				20.9 (25.1)	4×10^{-5}
		$MeSiF_3 + (H_2O)_2 \rightarrow MeSiF_2OH + HF-H_2O$			
DFT1	−23.0 (−19.3)	64.9	−6.3	19.3 (20.9)	2.2×10^{-4}
DFT2	−23.9 (−20.1)	56.9			
		$MeSiF_2OH + (H_2O)_2 \rightarrow MeSiF(OH)_2 + HF-H_2O$			
DFT1	−20.5	67.0	−15.5	31.0 (32.6)	2×10^{-6}
		$MeSiF(OH)_2 + (H_2O)_2 \rightarrow MeSi(OH)_3 + HF-H_2O$			
DFT1	−25.1	72.0	−22.6	36.0 (37.7)	2.6×10^{-7}
		$HSiF_3 + HF-H_2O \rightarrow HSiF_2OH + (HF)_2$			
DFT1	−6.3	66.1		52.7 (46.0)	8.5×10^{-9}
DFT2	−6.3	66.1		54.0 (47.7)	
		$MeSiF_3 + HF-H_2O \rightarrow MeSiF_2OH + (HF)_2$			
DFT1	−5.0	76.2		56.1 (49.4)	2.2×10^{-9}
DFT2				56.9	

[a] Relative energies (0 K) and Gibbs free energies (298 K) are given in kilojoules per mole. All substrate energies were set at 0.0 kJ/mol. [b] DFT1 = B3LYP/6-311+G(2d,p)//HF/6-31+G(d); DFT2 = B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p). [c] BSSE-corrected values are given in parentheses. [d] ΔG^{298} values are given in parentheses. [e] $K = e^{-\Delta G/RT}$.

TABLE 3: Relative Energies and Gibbs Free Energies for the Stepwise Hydrolysis of $HSiF_3$ in Water[a]

reaction	RC1	TS	products (ΔG^{298})[b]	K[c]
$HSiF_3 + H_2O \rightarrow HSiF_2OH + HF$	−11.3	100.4	13.0 (7.1)	0.057
$HSiF_2OH + H_2O \rightarrow HSiF(OH)_2 + HF$	−15.5	103.0	23.0 (20.1)	3.0×10^{-4}
$HSiF(OH)_2 + H_2O \rightarrow HSi(OH)_3 + HF$	−13.4	87.9	31.4 (29.7)	6.2×10^{-6}

[a] Relative energies (0 K) and Gibbs free energies (298 K) are given in kilojoules per mole and were determined by the IEFPCM/B3LYP/6-311+G(2d,p)//HF/6-31+G* method. All substrate energies were set at 0.0 kJ/mol. [b] ΔG^{298} values are given in parentheses. [c] $K = e^{-\Delta G/RT}$.

involving water dimer. It is also more unfavorable than the latter reaction, since $HF-H_2O$ complex produced in reaction 10 is stronger than the HF dimer produced in reaction 11 [G3B3 calculated ΔG values for complex formation are −0.6 and 20.9 kJ/mol for $HF-H_2O$ and $(HF)_2$, respectively]. No evidence for acid catalysis is observed in this system. It should be mentioned, however, that this model reaction is still far from the conditions occurring in the condensed phase.

Influence of Solvent. To estimate the effect of solvent on the hydrolysis of fluorosilanes, SCRF PCM calculations were performed for the same model systems. The results are presented in Table 3. Geometries of intermediate structures are similar to those calculated in the gas phase. A significant difference is that the transition state in water is more advanced than in the gas phase; that is, the forming Si−O bond is shorter by 0.03−0.04 Å while the distance between Si and leaving fluorine is longer by 0.15−0.17 Å. Details of the discussed structures can be found in the Supporting Information. Energy barriers for hydrolysis in water are lower than in the gas phase, although not as low as for the reaction with water dimer. It would be interesting to see how the increasing number of water molecules participating in the reaction affects the energy barrier within the SCRF approximation. This should model conditions of the reaction in solution more closely. Unfortunately, the optimization procedure for hydrolysis of fluorosilanes by a water dimer failed due to convergence problems.

Hydrolysis of trifluorosilane in aqueous medium is less unfavorable than in the gas phase, particularly the first stage of the reaction (reaction 6). The equilibrium constant of 0.057 corresponds roughly to 80% conversion of the substrate, if a water/silane proportion of 100:1 (mol/mol) is assumed, which is definitely too high.

Comparison with Chlorosilanes. Hydrolysis of chlorosilanes was thoroughly studied by theoretical methods.[29−31] There was no need to repeat these calculations. For the purpose of direct comparison only, we have recalculated the reaction system $HSiCl_3 + H_2O$, since the previous calculations were performed by methods different from that applied here. We found that the energies obtained with the B3LYP/6-311+G(2d,p)//HF/6-31+G(d) (DFT1) method are in good agreement with those obtained earlier with the MP4//MP2/6-31G* methods (Table 4).[29] They agree also with B3LYP/6-311G(2d,2p) calculations for the $SiCl_4 + H_2O$ system.[31] For example, total free energy change at B3LYP/6-311G(2d,2p) for the first step of $SiCl_4$ hydrolysis is $\Delta G = -22.2$ kJ/mol, compared to −23.0 kJ/mol for $HSiCl_3 + H_2O$ reaction at the DFT1 level.

Since the Si−Cl bond is weaker than the Si−O bond, hydrolysis of chlorosilanes is exothermic. As was discussed above, in contrast to fluorosilanes, the energy barrier decreases (and the reaction rate is expected to increase) with the degree of substitution by OH, leading finally to the product of full hydrolysis, $RSi(OH)_3$.

Condensation. There are two possible reactions leading to siloxane: homofunctional condensation of silanol groups and heterofunctional condensation of silanol with fluorosilane

TABLE 4: Relative Energies and Gibbs Free Energies for the Stepwise Hydrolysis of $HSiCl_3$[a]

method[b]	RC1	TS	RC2	products (ΔG^{298})[c]	K[d]
		$HSiCl_3 + H_2O \rightarrow HSiCl_2OH + HCl$			
DFT1	−8.4	95.4	−29.7	−4.6 (−23.0)	1700
G3B3				−19.3 (−18.4)	
MP4	−24.3	122.6	−42.3	−23.9	
		$HSiCl_2OH + H_2O \rightarrow HSiCl(OH)_2 + HCl$			
DFT1	−7.1	67.7	−28.5	−11.3 (−16.7)	520
G3B3				−16.3 (−15.5)	
MP4	−22.2	84.5	−41.4	−13.8	
		$HSiCl(OH)_2 + H_2O \rightarrow HSi(OH)_3 + HCl$			
DFT1	−32.2	66.5	−27.6	−6.3 (−10.9)	95
G3B3				−12.6 (−11.3)	
MP4	−28.9	79.1	−41.4	−13.4	
		$HSiCl_3 + (H_2O)_2 \rightarrow HSiCl_2OH + HCl\text{-}H_2O$			
DFT1	−11.7	43.1		−16.7 (−28.5)	5500
G3B3				−25.9 (−21.3)	
MP4		33.5			

[a] Relative energies (0 K) and Gibbs free energies (298 K) are given in kilojoules per mole. All substrate energies were set at 0.0 kJ/mol. [b] DFT1 = B3LYP/6-311+G(2d,p)//HF/6-31+G(d); MP4 = MP4//MP2/6-31G*.[29] [c] ΔG^{298} values are given in parentheses. [d] $K = e^{-\Delta G/RT}$ for ΔG^{298} calculated at G3B3.

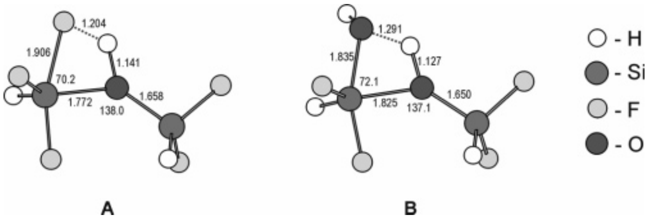

Figure 5. HF/6-31+G* optimized structures of transition states for heterofunctional condensation of $HSiF_3$ with HF_2SiOH (A) and homofunctional condensation of HF_2SiOH (B). Bond lengths are given in angstroms, and angles are given in degrees.

TABLE 5: Relative Energies and Gibbs Free Energies for the Condensations $HSiF_2OH + HSiF_3$ and $HSiCl_2OH + HSiCl_3$[a]

method[b]	TS	products (ΔG^{298})[c]	K[d]
		$2HSiF_2OH \rightleftharpoons (HSiF_2)_2O + H_2O$ (homofunctional)	
DFT1	118.0	−2.9 (−2.5)	2.8
G3B3	140.6	−23.0 (−24.7)	2.1×10^4
SCRF		13.6	
		$HSiF_3 + HSiF_2OH \rightleftharpoons (HSiF_2)_2O + HF$ (heterofunctional)	
DFT1	121.8	31.0 (32.6)	1.9×10^{-6}
G3B3	141.0	9.2 (6.7)	0.067
SCRF		26.7	
		$2HSiF_3 + H_2O \rightleftharpoons (HSiF_2)_2O + 2HF$	
DFT1		64.4 (59.4)	3.8×10^{-11}
G3B3		41.4 (38.5)	1.8×10^{-7}
SCRF		39.8 (36.0)	4.9×10^{-7}
		$2HSiCl_2OH \rightleftharpoons (HSiCl_2)_2O + H_2O$ (homofunctional)	
DFT1	134.8	3.8 (5.8)	0.09
CBS-QB3		−23.4 (−10.9)	80
G3B3		−17.2 (−20.5)	3900
		$HSiCl_3 + HSiCl_2OH \rightleftharpoons (HSiCl_2)_2O + HCl$ (heterofunctional)	
DFT1	118.4	−11.7 (−16.7)	860
CBS-QB3		−39.8 (−26.4)	4.2×10^4
G3B3		−36.8 (−38.9)	6.6×10^6
		$2HSiCl_3 + H_2O \rightleftharpoons (HSiCl_2)_2O + 2HCl$	
DFT1		−26.8 (−40.2)	1.1×10^6
CBS-QB3		−56.5 (−41.2)	2.1×10^6
G3B3		−56.9 (−57.3)	1.1×10^{10}

[a] Relative energies (0 K) and Gibbs free energies (298 K) are given in kilojoules per mole. All substrate energies were set at 0.0 kJ/mol. [b] DFT1 = B3LYP/6-311+G(2d,p)//HF/6-31+G(d); SCRF = DFT1 in water. [c] ΔG^{298} values are given in parentheses. [d] $K = e^{-\Delta G/RT}$.

(Figure 5). The results of calculations for both reactions are presented in Table 5.

Compound methods (CBS, G3) give values of thermodynamic parameters lower than DFT1 by 17−23 kJ/mol, suggesting more advanced condensation. One of the reasons for this discrepancy may be that correct treatment of siloxanes requires correlation methods. Unlike the heterofunctional condensation $HSiF_3$ + $HSiF_2OH$, homofunctional condensation of $HSiF_2OH$ is thermodynamically favorable, with equilibrium constant in the range of 2.8 (DFT1)−21 000 (G3B3) (Figure 5). Rates of both reactions, estimated from energy barrier heights, should be comparable. Activation energy for condensation is higher than for hydrolysis, both in the gas phase and in water (Tables 3 and 5), suggesting that, if entropy factors are comparable, condensation should be slower than hydrolysis. In the case of chlorosilanes, both condensations are thermodynamically favored, although heterofunctional condensation is more privileged, both thermodynamically and kinetically. It should be kept in mind, however, that this result refers to noncatalyzed reaction, while in acidic conditions homocondensation of silanols is strongly accelerated.[18] Energy barriers for SiF and SiCl condensations are similar, which suggests that all reactions have comparable rates in the gas phase.

The equilibrium constant for the overall hydrolysis/condensation of $HSiF_3$ in water is higher compared to the reaction in the gas phase, 4.9×10^{-7} (3.8×10^{-11} in the gas phase, Table 5). Nevertheless, this value corresponds to only ca. 2.3% of disiloxane $(HF_2Si)_2O$, if 100-fold excess of water relative to silane in the reaction mixture is assumed. This result agrees with experimental observations.[6] Further hydrolysis of $(HF_2Si)_2O$ was examined for the first step of substitution (reaction 12) to check whether the siloxane fragment influences the reaction energetics. The DFT1 energy (at 0 K) and Gibbs energy values are 39.3 and 37.2 kJ/mol, respectively, and the barrier for the reaction $\Delta E^{\ddagger} = 100$ kJ/mol, showing that there is no significant difference in thermodynamics and kinetics between hydrolysis of $SiHF_3$ and of $(HF_2Si)_2O$.

$$(HF_2Si)_2O + H_2O \rightarrow HF_2SiOSiHF(OH) \qquad (12)$$

When it is taken into account that the equilibrium concentration of disiloxane $(HF_2Si)_2O$ is small, further hydrolysis is expected to be negligible.

Conclusions

Hydrolysis of fluorosilanes is highly endothermic. The unfavorable equilibrium position is somewhat shifted toward the products, when the condensation of silanol is considered. The barriers for consecutive hydrolysis steps are very similar, indicating that the electrophilic assistance of the OH group to the leaving F is insignificant (in contrast to chlorosilanes). The Gibbs free energy increases for consecutive reaction steps, which means that hydrolysis of subsequent fluorine atoms in trifluorosilanes is thermodynamically more unfavorable than substitution of the first fluorine atom. Such thermodynamics contrasts with hydrolysis of chlorosilanes, where each subsequent step is more facile, leading first to the product of full hydrolysis, $RSi(OH)_3$, which further undergoes slower condensation.[35]

No significant difference in thermodynamics of hydrolysis is predicted between $HSiF_3$ and $MeSiF_3$. The corresponding energy barriers for $MeSiF_3$ are higher by ca. 4 kJ/mol, which may reflect the steric hindrance of the methyl group.

Hydrolysis by a water dimer has lower activation energy than that involving a single H_2O molecule (as was observed for chlorosilanes[29−31] and siloxanes[32]). This can be explained by the strain release in the transition state compared to simple bimolecular hydrolysis and by the cooperativity of hydrogen bonds, which facilitates proton transfer from water molecule acting as a nucleophile to the leaving fluoride anion. The reaction is also less unfavorable thermodynamically, due to a high binding energy of the $HF-H_2O$ complex.

SCRF calculations suggest that hydrolysis of trifluorosilane in aqueous medium is faster and thermodynamically more favorable than in the gas phase. Unlike the heterofunctional condensation $HSiF_3 + HSiF_2OH$, homofunctional condensation of $HSiF_2OH$ is thermodynamically favorable. Activation energies for both reactions are very similar but are higher than those for hydrolysis. Neutral condensation is thus predicted to be slower than hydrolysis. However, homocondensation of silanol is known to be strongly catalyzed by acids.

The equilibrium constant for the overall hydrolysis/condensation of $HSiF_3$ in water is higher compared to the reaction in the gas phase. Nevertheless, only ca. 2.3% of disiloxane $(HF_2Si)_2O$ is predicted to exist in the equilibrium mixture, if 100-fold excess of water relative to silane is assumed. Further hydrolysis of disiloxane is strongly unfavorable. Thus, the main product of trifluorosilane hydrolysis (and condensation) is expected to be disiloxane $(HF_2Si)_2O$. This result supports the experimental observations.[6]

Supporting Information Available: Coordinates and absolute energies for all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Koinuma, H.; Manako, T.; Natsuaki, H.; Fujioka, H.; Fueki, K. *J. Non-Cryst. Solids* **1985**, *77*, 801.

(2) Matsuda, A.; Yagii, K.; Kaga, T.; Tanaka, K. *Jpn J. Appl. Phys.* **1984**, *23*, 2576.

(3) Nakagawa, S.; Shibayama, T.; Ryokawa, A.; Itoh, H. U.S. Patent 6,770,253, 2004.

(4) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(5) Nakadaira, Y.; Ohara, K.; Sakurai, H. *J. Organomet. Chem.* **2002**, *309*, 247.

(6) Pietschnig, R.; Merz, K. *Organometallics* **2004**, *23*, 1373.

(7) Hacker, N. P. U.S. Patent 6,838,124, 2005.

(8) Kunai, A.; Ohshita, J. *J. Organomet. Chem.* **2003**, *686*, 3.

(9) Zhang, Q.; Wang, S.; Wang, C.; Gu, Y. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4280.

(10) Ignatov, S. K.; Sennikov, P. G.; Chuprov, L. A.; Razuvaev, A. G. *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 837.

(11) Karpfen, A. *J. Mol. Struct. (THEOCHEM)* **2004**, *710*, 85.

(12) Becerra, R.; Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley-Interscience: New York, 1998; p 153.

(13) Walsh, R. In *Silanes and Silicones (Gelest Catalog)*; Arkles, B., Larson G., Ed.; Gelest, Inc.: Morrisville, NJ, 2004; p 187 (on-line version http://www.gelest.com/Library).

(14) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1996.

(15) Sagitova V. G.; Chernyak, V. I. *Zh. Obshch. Khim.* **1983**, *53*, 397.

(16) (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. (b) Ring, M. A.; O'Neal, H. E.; Kadhim, A. H.; Jappe, F. *J. Organomet. Chem.* **1966**, *5*, 124.

(17) Hyde, J. F.; Brown P. L.; Smith, A. L. *J. Am. Chem. Soc.* **1960**, *82*, 5854.

(18) Chojnowski, J.; Cypryk, M. Synthesis of linear polysiloxanes. In *Silicon-Containing Polymers*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000; p 1.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford CT, 2004.

(20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(21) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976.

(22) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

(23) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(24) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(25) Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct. (THEOCHEM)* **1999**, *464*, 211.

(26) Heath, G. A.; Thomas, L. F.; Sheridan, J. *Trans. Faraday Soc.* **1954**, *50*, 779.

(27) Rempfner, B.; Oberhammer H.; Auner, N. *J. Am. Chem. Soc.* **1986**, *108*, 3893.

(28) Lukevits, E.; Pudova, O.; Strkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis Horwood Ltd: Chichester, U.K., 1989; p 231.

(29) Kudo, T.; Gordon, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 11432.

(30) Kudo, T.; Gordon, M. S. *J. Phys. Chem. A* **2002**, *106*, 11347.

(31) Ignatov, S. K.; Sennikov, P. G.; Razuvaev, A. G.; Chuprov, L. A.; Schrems, O.; Ault, B. S. *J. Phys. Chem. A* **2003**, *107*, 8705.

(32) Cypryk, M.; Apeloig, Y. *Organometallics* **2002**, *21*, 2165.

(33) Corriu, R. J. P.; Guérin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265.

(34) Ignatyev, I. S.; Schaefer, H. F. *J. Phys. Chem. A* **2001**, *105*, 7665.

(35) Yamamoto, S.; Yasuda, N.; Ueyama, A.; Adashi, H.; Ishikawa, M. *Macromolecules* **2004**, *37*, 2775.