Water Complexes and Hydrolysis of Silicon Tetrafluoride in the Gas Phase: An ab Initio Study

Stanislav K. Ignatov and Petr G. Sennikov

Intstitute of High-Purity Substances of RAS, ul. Tropinina, 49, Nizhny Novgorord 603600, Russia

Bruce S. Ault*

Department of Chemistry, University of Cinncinnati, Cincinnati, Ohio 45221

Alexander A. Bagatur'yants

Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7a, Moscow 117421, Russia

Igor V. Simdyanov, Alexey G. Razuvaev, and Eugene Ju. Klimov

University of Nizhny Novgorod, pr. Gagarina 23, Nizhny Novgorod 603600, Russia

Odd Gropen

Department of Chemistry, Faculty of Science, University of Tromsø, 9037 Tromsø, Norway

Received: June 15, 1999

An ab initio study of the structure, binding energies, electronic distribution, vibrational frequencies, and thermodynamic parameters of possible gas-phase complexes of silicon tetrafluoride with water (1:1, 2:1, and 1:2) in different conformations has been performed at the RHF, B3LYP, MP2, and MP4(sdq) levels with a variety of basis sets up to cc-pVTZ. On this basis, the thermodynamic stability, assignment of observed infrared bands of SiF_4/H_2O adducts in matrixes and in the gas phase, and activation energies of the elementary reactions leading to polyhydroxy derivatives and siloxane are discussed. The most thermodynamically stable structure is a 1:1 complex with the most accurate estimate of the binding energy of 2.7 kcal/mol. This complex is characterized by a small amount of electron transfer from the water molecule to silicon tetrafluoride and by small participation of the silicon d-orbitals in the coordination bond. A single stable conformation has been found for complex $2SiF_4{\cdot}H_2O$ whereas the complex $SiF_4{\cdot}2H_2O$ can exist in two conformations (distorted octahedral symmetry), distinguished by positions of the water molecules. The energetically preferred conformation of $SiF_4{\cdot}2H_2O$ is that with the water molecules in cis positions of an octahedron. The activation energy for the hydrolysis of first Si−F bond is 21 kcal/mol. The most thermodynamically preferred product at the first stages of hydrolysis is the hexafluorodisiloxane $SiF_3{-}O{-}SiF_3$ (activation energy 30 kcal/mol) rather than polyhydroxy derivatives.

Introduction

Silicon halogenide chemistry and, in particular, silicon tetrafluoride SiF_4 gas-phase association play a crucial role in many modern technologies (fiber optics, high pure substances technology, and microelectronics) and have been intensively studied by both experimental[1−10] and theoretical[11−14] methods. The SiF_4 molecule has T_d symmetry and has the electron configuration $(1a)^2(1t_2)^6(2a)^2(2t_2)^6(1e)^4(3t_2)^6(t_1)^6$ in the ground state. It is frequently assumed[1,8] that as in other silicon compounds, a substantial part of the formation of chemical bonds by SiF_4 involves the vacant 3d-orbitals of the central silicon atom; at the same time it has been pointed out[10] that σ-bonding with electron-donor molecules with the participation of 3d-orbitals is mainly due to strong electronegative groups located near the silicon atom.

Among the complexes of silicon tetrafluoride, strong adducts with organic ligands, containing a nitrogen atom, have been studied in the most detail.[1,2] The processes of weak gas-phase complexation of SiF_4 with oxygen-containing donors, including those with water, are considered in the literature to a lesser degree.[3−8] Meanwhile, investigation of molecular interactions in the silicon tetrafluoride−water system is important from the point of view of understanding the hydrolysis mechanism of this substance. Oxygen- and hydrogen-containing products even of the partial hydrolysis of SiF_4 in the presence of traces of moisture are undesirable while using silicon tetrafluoride in semiconductor fabrication and in production of preforms for silica optical fibers.[8] A number of papers have been devoted to the investigation of the process of SiF_4 hydrolysis in aqueous solution (see e.g. refs 1, 9, and 10 and references therein). Usually, it is considered that under these conditions the reaction results in the formation of a fluorosilicate and a hydrated silicon dioxide or of siloxanes with different composition and hydrogen fluoride. It was assumed[1] that in the initial step of hydrolysis a hexafluoro diaqua complex is formed that is then dissociated with formation of a hydroxonium ion and subsequent transformations. This scheme is hardly probable in the gas phase with

10.1021/jp9919819 CCC: $18.00

TABLE 1: Geometric Parameters of Complex I Optimized at the Various Levels of Theory (Bond Lengths in Å; Angles in Deg) with Atom Numbering Corresponding to Figure 1

geometry param	B3LYP/ 6-311G(d,p)	MP2/ 6-311G(d,p)	B3LYP/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)	MP2/ 6-311++G(2d,p)	MP2/ cc-pVTZ
SiF_4						
r(Si−F1)[a]	1.581	1.583	1.584	1.587	1.569	1.572
H_2O						
r(O−H)[b]	0.962	0.959	0.962	0.960	0.963	0.959
H−O−H[c]	103.8	102.3	105.1	103.4	104.6	103.5
$SiF_4\cdot H_2O$						
r(Si···O)	2.549	2.596	2.770	2.786	2.838	2.820
r(O−H)	0.963	0.960	0.963	0.961	0.964	0.960
r(Si−F1)	1.596	1.597	1.595	1.598	1.578	1.581
r(Si−F2)	1.591	1.590	1.588	1.590	1.571	1.576
r(Si−F3,F4)	1.587	1.586	1.586	1.587	1.569	1.573
r(H−F)[d]	2.848	2.884	3.224	3.036	3.060	3.073
H−O−H	105.6	103.8	106.0	104.3	105.1	104.2
Si−O−H	114.7	115.2	120.4	120.4	118.7	112.5

[a] The experimental value is 1.552 Å.[19] [b] The experimental value is 0.957 Å.[20] [c] The experimental value is 104.5°.[20] [d] The shortest distance H−F.

a low concentration of water. Earlier,[6] we used infrared spectroscopy to prove that along with hexafluorodisiloxane, Si_2F_6O, the hydroxy derivatives $SiF_{4-x}(OH)_x$ are formed in the reaction of gaseous SiF_4 with traces of water. It was impossible to determine the formation of any intermediates within the framework of this technique. On the other hand, the use of IR spectroscopy in low-temperature (12 K) argon and nitrogen matrixes containing water and silicon tetrafluoride allowed to one of us (B.S.A.) to observe the 1:1 complex $SiF_4\cdot H_2O$, presumably as a result of partial transfer of electron density from the water molecule to silicon tetrafluoride.[4]

The purpose of this paper is a detailed consideration of the structure and energetics of the complexes formed by silicon tetrafluoride and water with composition of 1:1, 1:2, and 2:1 using ab initio calculations. On the basis of these data, thermodynamic and activation parameters for possible elementary steps of the interaction of the molecules SiF_4 and H_2O have been studied with the aim of obtaining the most complete description of the actual mechanism of hydrolysis of silicon tetrafluoride and to interpret the available experimental data.

Method of Calculations

All the ab initio RHF and MP2 calculations have been performed using the GAMESS program.[15] Calculations at the B3LYP and MP4(sdq) level were carried out using the GAUSSIAN94 package.[16] Geometry optimization and saddle point location have been performed without any constraints. All of the stationary points have been characterized by the Hessian calculations at the RHF and B3LYP level, and some key stationary points, at the MP2 level. Basis sets were varied in wide ranges from 6-311G(d) to 6-311G++(2d,p) and cc-pVTZ. The 6d Gaussian functions were used for the RHF and MP2 calculations whereas the 5d functions were used at the B3LYP level. The basis set superposition errors (BSSE) were estimated with the counterpoise correction method.

Results and Discussion

1. Structure and Energies of Complexes of SiF_4 with H_2O. As the first elementary step in the hydrolysis of silicon tetrafluoride, we have studied the formation of three initial complexes of SiF_4 with water, of the compositions 1:1 (complex **I**), 2:1 (complex **II**), and 1:2 (complex **III**):

$$SiF_4 + H_2O \rightarrow \underset{\mathbf{I}}{SiF_4\cdot H_2O}$$

$$SiF_4\cdot H_2O + SiF_4 \rightarrow \underset{\mathbf{II}}{2SiF_4\cdot H_2O}$$

$$SiF_4\cdot H_2O + H_2O \rightarrow \underset{\mathbf{III}}{SiF_4\cdot 2H_2O}$$

The structures of complexes **I**−**III** were optimized at the RHF, B3LYP, and MP2 levels using 6-311G(d,p) and 6-311G++G(d,p) basis sets. Additional MP2 calculations using the extended basis sets were performed for complex **I**. We located a single true PES minimum each for complexes **I** and **II**, and two ones for complex **III**. Table 1 lists the geometric parameters for complex **I** optimized at various levels of theory together with a geometry of parent SiF_4 and H_2O molecules, and Table 2 shows the optimized geometric parameters of complexes **II** and **III**. Figure 1 shows the structure of these complexes.

*Complex $SiF_4\cdot H_2O$ (**I**).* Although for complex **I** the hydrogen-bonded structure Si−F···H−OH seems intuitively to be possible, the single structurally stable conformation was of C_s symmetry with a Si−O donor−acceptor bond (Figure 1a). The species with one and two hydrogen bonds F···H but without a Si−O bond ($F_3Si{-}F\cdots H{-}OH$ and $F_2Si<^{F\cdots H}_{F\cdots H}>O$) undergo nonactivated rearrangement to the structure presented in Figure 1a. As is shown in Figure 1a, the hydrogen atoms of water molecule are tilted toward the SiF_4 molecule. The conformation of complex **I** with a nontilted orientation of water molecule is not stable one and is a transition state between two tilted stable conformations. Thus, the structure of complex **I** corresponds to a distorted trigonal bipyramid. It is in agreement with known results on quantum-chemical studies of related systems, $SiF_4\cdot NH_3$[11,12] and $BF_3\cdot NH_3$,[17] as well as with results of the above-mentioned IR matrix isolation study of the SiF_4/H_2O adduct.[4]

Although the bipyramidal structure is an inherent feature of complex **I** for all levels of theory, the calculated Si−O bond length is strongly influenced by the basis set used. It is common knowledge that the correct description of the weakly bonded complexes may be achieved by supplementing the basis set with diffuse functions. As follows from Table 2, using diffuse functions results in increasing the Si−O bond length by 0.2 Å (7%) both at the MP2 and B3LYP levels. However, further

TABLE 2: Geometric Parameters of Complexes II and III Optimized at the Various Levels of Theory (Bond Lengths in Å; Angles in deg) with Atom Numbering Corresponding to Figure 1

geometry param	B3LYP/ 6-311G(d,p)	MP2/ 6-311G(d,p)	B3LYP/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)
		$2SiF_4 \cdot H_2O$		
r(Si1⋯O)	2.777	2.789	2.907	2.886
r(Si2⋯O)	2.835	2.858	2.942	2.916
r(O−H)	0.964	0.961	0.964	0.963
r(Si−F)	1.580−1.590	1.577−1.585	1.582−1.591	1.584−1.594
r(H−F)[a]	2.686	2.721	2.793	2.813
H−O−H	105.7	104.0	105.6	104.1
Si−O−Si	109.2	108.0	110.2	106.1
		$SiF_4 \cdot 2H_2O$ (Structure A)		
r(Si⋯O)	2.090	2.054	2.108	2.066
r(O−H)	0.965	0.963	0.966	0.965
r(Si−F1,F2)	1.645	1.646	1.647	1.651
r(Si−F3,F4)	1.626	1.629	1.630	1.633
r(H−F)[a]	2.390	2.365	2.416	2.387
H−O−H	108.2	106.7	108.3	106.7
Si−O−H	108.9	108.3	110.3	109.4
O−Si−O	83.8	83.6	83.1	82.9
F1−Si−F2	153.9	155.5	153.6	155.3
F3−Si−F4	102.4	101.9	102.4	102.1
		$SiF_4 \cdot 2H_2O$ (Structure B)		
r(Si⋯O)	1.944	1.932	1.943	1.933
r(O−H)	0.966	0.964	0.967	0.966
r(Si−F1,F2)	1.666	1.664	1.671	1.671
r(Si−F2,F4)	1.649	1.648	1.654	1.654
r(H−F)[a]	2.356	2.350	2.378	2.378
H−O−H	110.3	108.6	110.4	108.6
O−Si−O	177.0	177.5	177.8	177.7
F1−Si−F3	170.8	171.9	171.1	172.0
Si−O−H	111.0	110.2	112.3	111.5

[a] The shortest distance H−F.

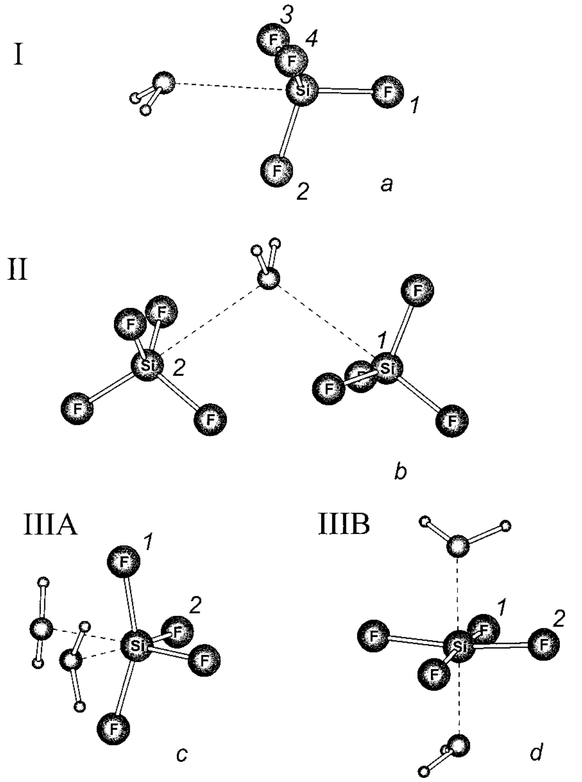

Figure 1. Calculated structures of complexes **I**−**III**.

TABLE 3: Binding Energies of Complex I Calculated at the Various Levels of Theory and Energies Corrected by the Basis Set Superposition Error (kcal/mol)

level of theory	calcd binding energy	binding energy corrd by BSSE
RHF/6-311G(d,p)	5.8	−2.1
B3LYP/6-311G(d,p)	7.5	2.9
B3LYP/6-311++G(d,p)	4.3	2.7
MP2/6-311G(d,p)	7.3	−0.2
MP2/6-311G(df,p)// MP2/6-311G(d,p)	7.4	2.0
MP4(sdq)/6-311G(df,p)// MP2/6-311G(d,p)	7.7	2.7
MP2/6-311G(3df,2pd)// MP2/6-311G(d,p)	6.9	2.3
MP2/6-311+G(d,p)	5.4	2.8
MP2/6-311++G(d,p)	5.4	2.7
MP2/6-311G++(2d,p)	4.6	2.7
MP2/cc-pVTZ	4.9	2.7

extending the basis sets has only small effect on this geometric parameter. The use of the split d-functions and extended cc-pVTZ basis sets at the MP2 level results only in 1−2% changes in the Si−O bond length. Other geometric parameters depend significantly less on the basis set except the Si−F bond length. This distance is typically overestimated both in the parent SiF_4 molecule and in the complex. This overestimation has little effect on the structure and binding energy of complex **I** and may be sufficiently reduced by the using two sets of d-functions on the silicon atom. Therefore, the MP2/6-311G++(2d,f) calculations result a noticeable decrease of the Si−F bond length.

The calculated binding energies of complex **I** are presented in Table 3 together with the BSSE-corrected values. As shown from the table, the calculated values are strongly influenced by the level of theory. However, the BSSE-corrected values converge rather fast with the extended basis sets. Similar to the geometric parameters, the use of the diffuse functions results in a significant improvement of the results. The BSSE-corrected binding energy value obtained at the MP2/6-311++G(d,p) level is 2.7 kcal/mol, and further extending the basis set does not result in noticeable energy changes. The use of a correlation

TABLE 4: Changes in the Mulliken Orbital Populations Due to the Comples I Formation Process at the MP2/6-311G(d,p) Level for First-Order MP2 Wave Function

AO's	Si	F1, F2	F3, F4	O	H	SiF_4	H_2O
			$SiF_4 \cdot H_2O$				
s	0.006	−0.003	−0.004	0.006	0.024	−0.008	0.054
p	0.018	−0.020	−0.008	−0.020	0.003	−0.038	−0.013
d	0.001	0.001	0.001	0.000		0.005	0.000
total	0.026	−0.022	−0.011	−0.015	0.028	−0.041	0.041
			$2SiF_4 \cdot H_2O$				
s	0.008	−0.003[a]	−0.005[a]	−0.002	0.030	−0.006	0.057
p	0.012	−0.012[a]	−0.003[a]	−0.025	0.004	−0.019	−0.016
d	0.001	0.001[a]	0.001[a]	0.001		0.004	0.001
total	0.021	−0.014[a]	−0.007[a]	−0.026	0.034	−0.021	0.042
			$SiF_4 \cdot 2H_2O$ (Structure A)				
s	0.095	−0.023	−0.017	0.015	0.062	0.014	0.140
p	0.109	−0.090	−0.069	−0.013	0.009	−0.208	0.005
d	−0.109	0.006	0.005	−0.004		−0.086	−0.004
total	0.095	−0.107	−0.081	−0.002	0.071	−0.280	0.140
			$SiF_4 \cdot 2H_2O$ (Structure B)				
s	0.109	−0.023	−0.023	0.032	0.082	0.017	0.190
p	0.153	−0.111	−0.086	−0.019	0.009	−0.240	0.000
d	−0.172	0.007	0.006	−0.007		−0.146	−0.007
total	0.091	−0.127	−0.103	0.007	0.091	−0.370	0.185

[a] Averaged values.

energy estimation other than MP2 (B3LYP or MP4SDQ) also has only a small effect on the BSSE-corrected binding energy values. However, the correlation energy plays rather important role in the process of complex formation (the 6-311G(d,p) BSSE-corrected energy estimated at the RHF level is −2.1 whereas the MP2 value is −0.2 kcal/mol). The BSSE-corrected binding energies obtained at the MP2/6-311++G(2d,p) and MP2/cc-pVTZ levels are 2.7 kcal/mol. This value can be considered as a most exact theoretical estimate of the binding energy for complex **I**. It should be noted that the same value is obtained at the MP2/6-311++G(d,p) level.

Thus, except for the Si−F bond lengths, the MP2/6-311++G-(d,p) results may be considered as a rather reliable description of the structure and binding energy of complex **I**. It is interesting that the B3LYP/6-311++G(d,p) results are very close to the MP2/6-311++G(d,p) results both for binding energies and for the molecular geometry. One may conclude that the binding between SiF_4 and H_2O units is only slightly influenced by the long-distance dispersion interactions.

Table 4 shows the changes in the Mulliken orbital populations and atomic charges in the process of formation of silicon tetrafluoride−water complexes calculated at the MP2 levels. The data collected for complex **I** indicate that the water molecule is a donor and SiF_4 is an acceptor of electron density but the value of charge transfer is only about 0.04e. The silicon and hydrogen atoms lose and the oxygen and fluorine atoms of the SiF_4 molecule gain the extra electron density. The d-AO's of the silicon atom as well as of d-AO's of O and F and p-AO of H take only a negligible part in the complex formation process. The main part of the electron density is redistributed between the s- and p-AO's of Si, O, F atoms and s-AO's of hydrogen. Thus, the binding between silicon tetrafluoride and water in complex **I** is a result of the coordination interaction without changes in the electronic and hybridization state and without significant redistribution of electron density.

*Complex $2SiF_4 \cdot H_2O$ (**II**).* Complex **II** forms by the addition of a second SiF_4 molecule to the oxygen atom of water in complex **I** (see Figure 1b). The single structurally stable conformation of complex **II** is characterized by a bent structure of C_s symmetry with an angle Si−O−Si of about 106°. The two molecules of SiF_4 in the ground state of complex **II** are rotated by about 60° relative to one another, and the fluorine atoms of the second SiF_4 molecule stay in positions between fluorine atoms of the first molecule. Because of this, the H···F distances between H_2O and SiF_4 molecules are nonequivalent. The H···F interaction between H_2O and the second coordinated SiF_4 molecule is more preferable than with first one. Thus, the elimination of an HF molecule from complex **II** should be easier than from complex **I**. As discussed below, this conclusion is supported by direct calculation of the activation energy.

Similar to complex **I**, the binding energy of complex **II** obtained at the MP2/6-311++G(d,p) level can be considered as a best estimated value. The comparison of the BSSE-corrected value for complex **II** (4.6 kcal/mol) and complex **I** (2.7 kcal/mol) shows that the addition of second SiF_4 molecule has about a 30% lesser energetic effect than the first one. The average binding energy value (2.3 kcal/mol) is only slightly less than in complex **I**, and the coordination bonds Si···O in these complexes are almost equivalent.

As may be concluded from Table 4, the electronic structure of complex **II** is also very similar to those of complex **I**. The only exception is that the SiF_4 charge is half that in complex **I**.

*Complex $SiF_4 \cdot 2H_2O$ (**III**).* Unlike complexes **I** and **II**, two structurally stable conformations were found for complex **III**. The ground state (energetically preferred conformation) is a distorted octahedral structure with H_2O ligands occupying cis positions (complex **IIIA**) (see Figure 1c). The symmetry group of the complex is C_{2v} with a 2-fold axis bisecting the angle O−Si−O. Another conformation (complex **IIIB**) is a slightly distorted octahedral structure of C_1 symmetry with two H_2O molecules occupying trans positions (see Figure 1d) and rotated by 90° each relatively another. Because of this rotation, the SiF_4 fragment is not planar. It should be noted that the more symmetric configurations of complex **IIIB** of C_s symmetry with the water molecules rotated by 0 or 180° relative to one another are not true minima and are transition states between the local minima of the distorted structure shown in Figure 1d.

Like complex **I**, in species **III** the H_2O molecules are tilted (in opposite directions) to the fluorine atoms in both conformations of the complex. Complex **IIIA** is formed by the nonactivated addition of a second water molecule to complex **I** whereas activation energy is required for the intermolecular rearrangement of complex **IIIA** to the **IIIB** structure.

The binding energies of complexes **I**−**III** are summarized in Table 5 for various levels of theory. Because of the strong structural rearrangement of the SiF_4 fragment and significant electronic redistribution (see below) in complexes **IIIA** and **IIIB**, the BSSE correction has no meaning in the case of these structures. We will use the calculated (not BSSE-corrected) values of the binding energy hereafter.

The energy difference between the trans and cis conformations is rather large (5.0 kcal/mol at the MP2/6-311++G(d,p) level). This is especially interesting taking into account that the trans-complex is frequently proposed as a primary intermediate in liquid-phase reactions of SiF_4.[1] Our calculations do not support this suggestion, at least for the gas-phase process. However, it should be noted that these energies and the relative stability of complexes might be strongly influenced by environmental effects (specific solvation, electric field of the solution, etc.).

In contrast with complexes **I** and **II**, significant changes in the electronic structure occur in the process of the formation of complex **III**. The data collected in Table 4 shows that a large amount of electronic density (0.28e for complex **IIIA** and 0.37e

TABLE 5: Binding Energy of Complexes I−III (kcal/mol)[a]

level of theory	$SiF_4·H_2O$ (**I**)	$2SiF_4·H_2O$ (**II**)	$SiF_4·2H_2O$ (**IIIA**)	$SiF_4·2H_2O$ (**IIIB**)
B3LYP/6-311G(d,p)	7.5 (2.9)	13.2 (4.0)	16.1	9.6
MP2/6-311G(d,p) (6d)	7.3 (−0.2)	13.7 (1.1)	17.1	10.9
B3LYP/6-311++G(d,p)	4.3 (2.7)	7.6 (4.6)	6.8	1.4
MP2/6-311++G(d,p) (6d)	5.4 (2.7)	11.0 (4.6)	11.0	6.0

[a] (BSSE-corrected energies are given in parentheses.)

TABLE 6: Relative Enthalpies and the Gibbs Free Energies (kcal/mol) of the Complexes I−III Calculated at the MP2/6-311++G(d,p) (B3LYP/6-311++G(d,p)) Levels

system	rel $\Delta H°$ (298)	rel ΔG		
		$T = 40$ K, $P = 10^{-6}$ atm	$T = 200$ K, $P = 3.5$ atm	$T = 298.15$ K, $P = 1$ atm
$2(SiF_4·H_2O)$	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
$2SiF_4·H_2O + H_2O$	+0.6[a] (+2.4)	+0.5[a] (+1.1)	+1.1[a] (+1.3)	+0.7[a] (+1.3)
$SiF_4·2H_2O$ (**A**) + SiF_4	−4.1 (+1.3)	−2.0 (+2.2)	+0.6 (+5.3)	+2.7 (+6.3)
$SiF_4·2H_2O$ (**B**) + SiF_4	+0.8 (+6.8)	+3.2 (+8.0)	+5.6 (+11.1)	+7.7 (+13.7)
parent ($2SiF_4 + 2H_2O$)	+2.7 (+4.3)	−0.7 (0.0)	−5.2 (−3.8)	−10.7 (−12.7)

[a] The values are calculated on the basis of the MP2/6-311++G(d,p) binding energies and the B3LYP/6-311++G(d,p) frequencies.

for complex **IIIB**) is transferred from the water molecules to silicon tetrafluoride. A large part of this amount is gained by the silicon d-orbitals, which play a crucial role in complex formation. Thus, the formation of the octahedral complexes **IIIA** and **IIIB** can be described in terms of strong sp^3d^2 hybridization after electron transfer to the silicon d-orbitals of SiF_4 molecule.

2. Relative Thermodynamic Stability of the Complexes I−III in the Gas Phase. It is well-known that, at these levels of theory, direct quantum chemical calculations of the absolute Gibbs free energies values of formation of chemical species result in the significant discrepancy with experimental data. On the other hand, one can estimate relative thermodynamic parameters for so-called isodesmic systems (systems with the same number of chemical bonds of given kind).[17] In our case, the systems $2SiF_4·H_2O$, $2SiF_4·H_2O + H_2O$, and $SiF_4·2H_2O + SiF_4$ may be considered as isodesmic (which can be supported by the fact that the Si···O bonds in complexes have approximately equal energies). We have calculated relative ΔH and ΔG values for these species at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. The BSSE corrections were taken into account for complexes **I** and **II**. The vibrational frequencies and moments of inertia of all species under consideration needed for the zero point energy (ZPE) and thermal corrections have been calculated after full geometry optimization at the corresponding level of theory except complex **II** whose frequencies are unavailable at the MP2 level. The thermodynamic functions for this complex were calculated using the MP2 binding energy and the B3LYP vibrational frequencies. All thermodynamic functions have been calculated in the "rigid rotor−harmonic oscillator" approximation. The effects of anharmonicity were partially taken into account at the B3LYP level where two low-frequency normal modes of complexes **I** and **II**, namely, rotation of H_2O around the Si−O bond in complex **I** ($\nu = 4$ cm^{-1}) and rotation of SiF_4 around the Si−Si direction in complex **II** ($\nu = 29$ cm^{-1}), were considered as pure internal rotations. At the MP2 level, these modes had rather high frequencies (above 100 cm^{-1}) and were considered as harmonic vibrations. The Gibbs free energies were calculated for three different conditions: standard conditions ($T = 298.15$ K, $P = 1$ atm); the typical conditions of low-temperature SiF_4 purification ($T = 200$ K, $P = 3.5$ atm); conditions near to the cryogenic matrix ($T = 40$ K, $P = 10^{-6}$ atm). The relative enthalpies and the Gibbs free energies for the system under consideration are listed in Table 6. The values are given relative to the system $2(SiF_4·H_2O)$ (a zero level) and characterize the relative thermodynamic stability of complexes **I**−**III** under corresponding conditions. To estimate ΔH and ΔG in the process of complex formation, the thermodynamic parameters of the parent system $SiF_4 + H_2O$ are also presented in Table 6. However, it should be noted that the parent molecules are not an isodesmic system relative to their complexes and direct comparison of thermodynamic values can give only a crude estimate of ΔH and ΔG of complex formation.

As follows from Table 6, both MP2 and B3LYP theories give similar results. The only exception is a stability of complex **IIIA**, which is the most stable system at low temperatures at the MP2 level but not at the B3LYP level. The reason for this discrepancy is that the BSSE correction value at the MP2 level is typically higher than at the B3LYP level (see Table 5). Because the BSSE correction was not taken into account for the complexes **III**, their stability relative to complexes **I** and **II** is likely to be overestimated at the MP2 level. Thus, the relative stability of complexes **I** and **III** estimated at the B3LYP level seems to be more correct. When one compares ΔH and ΔG between complexes **I** and **II** or between complexes **IIIA** and **IIIB**, the BSSE correction has approximately the same value and the B3LYP and MP2 results are each close to another.

From this point of view, one may conclude that the most stable system under consideration is complex **I**. Complex **II** is slightly higher both in ΔH and ΔG, but the difference between **I** and **II** is quite small. Finally, complexes **IIIA** and **IIIB** are higher in ΔG, and structure **IIIA** is more thermodynamically preferred over structure **IIIB**.

As follows from Table 6, this order in ΔG is retained over a wide range of temperatures and pressures. Thus, an equilibrium mixture of SiF_4 and H_2O should contain the species **I**, **II**, and **IIIA** in the approximate relative proportion $1:10^{-3}:10^{-13}$ under matrix isolation conditions and $1:10^{-1}:10^{-5}$ under standard conditions. This fact is in good agreement with the conclusions made on the basis of the study of the SiF_4/H_2O adduct in cryogenic matrixes.[4] This theoretical study also supports the suggestion that complex **I** is the most probable primary intermediate in the first step of SiF_4 hydrolysis.

The Gibbs free energy of the formation process for complex **I** (10.7 kcal/mol at MP2) is significantly greater than the difference in ΔG between different complexes under standard conditions but almost equal to zero at low temperatures (0.7 kcal/mol). Thus, the complex formation process is more probable under cryogenic conditions than under standard ones.

It should be noted that the above thermodynamic analysis should be considered with caution, especially for low temperatures when all the species are in the condensed state. The

TABLE 7: Calculated by MP2/6-311G++(d,p) (ν_{calc}) and Experimental Vibrational Frequencies (cm^{-1}) for Gas-Phase (ν_{gas}) and Matrix Isolation (ν_{matrix}) Conditions of SiF_4, H_2O, and Complex $SiF_4{\cdot}H_2O$, Shifts in Frequencies (ν, cm^{-1}) Due to Complex Formation, Calculated Intensities for $SiF_4{\cdot}H_2O$ (km/mol), and Corresponding Mode Assignment

ν_{matrix}[a] (ν_{gas}[b])			ν_{calc}				
$SiF_4 + H_2O$	$SiF_4{\cdot}H_2O$	ν	$SiF_4 + H_2O$	$SiF_4{\cdot}H_2O$	ν	I_{calc}	assignment
				97		9	ν(Si−O) + δ_s(Si−O−H)
				110		17	δ(O−Si−F1)
				112		2	δ(O−Si−F1)
				160		27	rotation H_2O around Si−O
(264)			256	228	−29	220	δ_s(Si−O−H)
(264)			256	240	−17	1	δ_{as}(Si−O−H) + δ(F−Si−F)
				266		31	δ_s(Si−O−H) + δ(F−Si−F)
				325		4	δ_{as}(Si−O−H) + δ(F−Si−F)
(388)			373	369	−3	78	$\delta_s(SiF_3)$(umbrella)
(388)			373	376	3	68	$\delta_s(SiF_3)$ + δ_s(Si−O−H)
(388)			373	386	14	76	$\delta_s(SiF_3)$ + δ_{as}(Si−O−H)
(801)			767	757	−10	0	$\nu_s(SiF_4)$
1023	984, 991[c]	−39, −32	999	955	−44	302	ν(Si−F1) + $\delta(SiF_3)$ (umbrella)
1023			999	998	−1	265	ν_{as}(F−Si−F)
1023			999	1009	10	267	ν_{as}(F−Si−F)
1593	1598	5	1630	1647	17	80	δ(H−O−H)
(3657)			3868	3858	−10	23	ν_s(H−O−H)
3730	3722	−8	3992	3980	−12	86	ν_{as}(H−O−H)

[a] Experimental frequencies from ref 4. [b] Experimental frequencies from ref 18. [c] Site splitting (see the text).

TABLE 8: Calculated by B3LYP/6-311G++(d,p) Frequencies (ν_{calc}, cm^{-1}) of SiF_4, H_2O, and Complexes I−III in Range 770−4000 cm^{-1} and the Shifts in Frequencies (ν, cm^{-1}) Due to Complex Formation in Comparison with Experimental ν Observed under Matrix Isolation Conditions

	$SiF_4{\cdot}H_2O$		$2SiF_4{\cdot}H_2O$		$SiF_4{\cdot}2H_2O$ (**IIIA**)		$SiF_4{\cdot}2H_2O$ (**IIIB**)		
$SiF_4 + H_2O$ ν_{calc}	ν_{calc}	ν	ν_{calc}	ν	ν_{calc}	ν	ν_{calc}	ν	obsrvd ν
999	949	−49	960, 970	−38, −28	808	−191	772	−227	−39, −32
999	993	−5	986, 989	−12, −10	872	−127	920	−79	
999	1005	6	1009, 1010	10, 12	939	−59	920	−79	
1602	1622	20	1625	22	1610, 1618	7, 16	1598, 1600	−4, −3	5
3818	3817	−1	3801	−17	3775, 3777	−42, −41	3760, 3762	−56, −57	
3923	3921	−3	3899	−24	3877, 3877	−46, −46	3862, 3862	−61, −61	−8

relative proportions among complexes **I**−**III** may also be strongly influenced by environmental or solvent effects. Finally, the difference between complexes **I** and **II** is comparable with the internal inaccuracy of quantum chemical calculations and seems to be too small to make an unambiguous conclusion on the relative proportions of complexes **I** and **II**. However, the reported results should reflect the main features in a real system and, in particular, the relative thermodynamic stability of complexes **I**−**III**.

3. Vibrational Frequencies of Complex $SiF_4{\cdot}H_2O$. Because complex **I** is a basic intermediate in the hydrolysis process of SiF_4 in gas phase, its infrared spectral features are of special interest. The reported infrared spectrum of the 1:1 SiF_4/H_2O adduct in argon and nitrogen matrixes[4] has bands at 984, 991, 1598, and 3722 cm^{-1} assigned to the $F_4Si{\cdots}OH_2$ coordinated complex formed in the initial step of reaction 1.

Table 7 (first three columns) shows the observed shifts in the vibrational frequencies of the SiF_4 and H_2O under matrix isolation conditions due to complex formation.[4] The next columns list the MP2/6-311++G(d,p) calculated frequencies of complex **I** in comparison with the frequencies of the parent molecules. The last two columns of the table list the calculated gas-phase intensities and assignments of the corresponding vibrations for complex **I**.

The calculated spectrum of $SiF_4{\cdot}H_2O$ complex has the frequencies of the H_2O subunit at 1647, 3858, and 3980 cm^{-1}. Only two of them were observed in the experimental spectrum at 1598 and 3722 cm^{-1} under matrix conditions. In range 900−1100 cm^{-1}, complex **I** has two calculated frequencies 998 and 1009 cm^{-1} near the band 999 cm^{-1} of parent SiF_4 and the new intense band at 955 cm^{-1} which is absent in a parent spectrum.

In the experimental spectrum of the SiF_4/H_2O adduct, two new bands at 984 and 991 cm^{-1} were observed. As proposed earlier,[4] these bands are due to site splitting of one vibration that probably corresponds to the Si−F stretching mode of SiF_4 at 1023 cm^{-1}. The observed shifts for these vibrations are −39 and −32 cm^{-1}. These values are in good agreement with the calculated value −44 cm^{-1} of the frequency shift due to complex **I** formation. Then, the calculated shifts for the O−H stretching and H−O−H bending modes (−12 and +17 cm^{-1}) are also in a good agreement with the observed shifts of these vibrations (−8 and +5 cm^{-1}). The calculated Si−F bands at 998 and 1009 cm^{-1}, which were not observed, are probably hidden by the strong absorption of unreacted parent SiF_4 between 1000 and 1025 cm^{-1}.

A similar picture takes place for the B3LYP/6-311++G(d,p) frequencies in range 770−4000 cm^{-1} presented in Table 8. Like the MP2 results, one of the B3LYP frequencies of complex **I** has a shift −49 cm^{-1} that is in good agreement with the observed band shift. The calculated frequencies of complexes **III** are far from the observed IR bands supporting the suggestion that these complexes are not preferred from thermodynamic point of view. However, complex **II** has two vibrations with shifts of −38 and −28 cm^{-1}, in very good agreement with the experimental shifts. On the basis of this fact, we propose that the observed two peaks at 984 and 991 cm^{-1} of SiF_4/H_2O adduct *may not* be a site splitting of one vibration but *may* be evidence of complex **II** formation in cryogenic matrixes. The complexes **I** and **II** are very close each to another in ΔG (see the previous section), and their relative concentration may be also comparable. In summary, a definitive decision as to whether the 991 cm^{-1} band is due to site splitting of the 984 cm^{-1} band or is

TABLE 9: Total Energies, Enthalpies, Gibbs Free Energies, and Equilibrium Constants of Hydrolysis Reactions Calculated at the MP2/6-311G(d,p) Level (kcal/mol)

reacn	ΔE_r	$\Delta H_r^\circ(298)$	$\Delta G_r^0(298)^a$	K_p^a
$2SiF_4 + 2H_2O \rightarrow 2SiF_3OH + 2HF$	+10.7	−0.9	+7.1 (+6.5)	$6.1 \cdot 10^{-6}$ ($1.7 \cdot 10^{-5}$)
$2SiF_4 + 2H_2O \rightarrow SiF_2(OH)_2 + SiF_4 + 2HF$	+11.5	−0.6	+10.3 (+8.1)	$2.6 \cdot 10^{-8}$ ($1.2 \cdot 10^{-6}$)
$2SiF_4 + 2H_2O \rightarrow SiF_3OSiF_3 + H_2O + 2HF$	+8.5	−0.3	+1.9 (+1.9)	$4.2 \cdot 10^{-2}$ ($4.2 \cdot 10^{-2}$)
$2SiF_4 + 2H_2O \rightarrow SiF_3OSiF_2OH + 3HF$	+13.1	−0.7	+5.8 (+4.6)	$5.9 \cdot 10^{-5}$ ($4.1 \cdot 10^{-4}$)

[a] Values in parentheses obtained when the rotational normal modes of the OH groups were considered as pure internal rotations.

due to a small amount of complex **II** cannot be made on the basis of the available information.

4. Thermodynamics and Infrared Frequencies of Hydrolysis Products. The thermodynamic stability of possible hydrolysis products of SiF_4 in the gas phase is of special interest from the point of view of theoretical limits for silicon tetrafluoride purification. We have considered two possible directions for the hydrolysis process: (1) the formation of hydroxy derivatives SiF_3OH, $SiF_2(OH)_2$ and their complexes with HF and H_2O; (2) formation of siloxane $SiF_3{-}O{-}SiF_3$, its complexes, and its further hydrolysis products ($SiF_3{-}O{-}SiF_2{-}OH$). The geometries of SiF_3OH, $SiF_2(OH)_2$, and $SiF_3{-}O{-}SiF_3$ and $SiF_3{-}O{-}SiF_2{-}OH$ have been optimized at the RHF/6-311G(d,p), MP2/6-311G(d,p), and B3LYP/6-311G(d,p) levels, and the relative Gibbs free energies have been calculated using a method analogous to those described in section 2. The SiF_3 and SiF_2OH groups are characterized by low-frequency (under 100 cm^{-1}) rotational modes which were considered as free internal rotations. The OH groups are typically characterized by rotational frequencies in range 100−200 cm^{-1} which were considered both as harmonic vibrations and as free internal rotations. Table 9 lists the total energies, ΔH, ΔG, and equilibrium constants of reaction for four hydrolysis processes calculated at the MP2/6-311G(d,p) level. The values in parentheses show the ΔG and K_p values obtained when some OH modes were considered as free internal rotations. As may be concluded, the most energetically preferred process is $SiF_3{-}O{-}SiF_3$ formation which is about 4−5 kcal/mol lower in the Gibbs free energy than SiF_3OH and 6−8 kcal/mol lower than $SiF_2(OH)_2$. Thus, the relative ratio between siloxane and monohydroxy and polyhydroxo derivatives in an equimolar gas-phase SiF_4/H_2O mixture under standard conditions should be between $1{:}10^{-4}{:}10^{-6}$ and $1{:}10^{-3}{:}10^{-4}$. Simultaneously, the ratio between $SiF_3{-}O{-}SiF_3$ and its hydrolysis products should be about $1{:}10^{-3}$ or $1{:}10^{-2}$. This is consistent with the available experimental observations. $SiF_3{-}O{-}SiF_3$ is a typical impurity in silicon tetrafluoride.[5,8] Recently, the $SiF3{-}O{-}SiF_2{-}O$ fragment was observed in the mass spectra of purified SiF_4.[6] To date, there is no direct experimental evidence of SiF_3OH and other low-molecular hydroxy derivatives in the hydrolytic mixture.

Recently obtained[6] FTIR spectra of gas-phase mixtures of SiF_4 and H_2O contain a broad, unstructured band at 3760 cm^{-1}. On the basis of the present study, we can assign this band to the different hydroxyl-containing species formed on further hydrolysis of $SiF_3{-}O{-}SiF_3$ (e.g. $SiF_3{-}O{-}SiF_2{-}OH$) and, probably, their complexes with H_2O and HF. Moreover, we cannot ruled out the temporary build up of SiF_3OH during the first steps of hydrolysis at low temperatures when the thermal energy is much less than the activation barrier for siloxane formation (see next section). The simultaneous existence of several OH-containing species with neighboring frequencies (various siloxane hydroxy derivatives, SiF_3OH, and their complexes) can explain the unstructured character and breadth of experimental band at 3760 cm^{-1}.

It should be noted that the calculated ΔG_r is strongly influenced by the method of accounting for anharmonicity. Moreover, the reactions presented in Table 9 are not isodesmic, and thus, the absolute values of the thermodynamic functions should be used with caution. However, these facts should not change the relative preferences of the reactions in principle, and $SiF_3{-}O{-}SiF_3$ remains the most preferred product as before.

5. Energies of activaTion at the Various Stages of Hydrolysis. It is interesting to estimate the activation energies of various elementary steps in the hydrolysis process. The formal scheme of the processes under consideration may be presented as follows. The first (common) step is hydrolysis of complex **I**, resulting in the formation of SiF_3OH in the form of $SiF_3OH{\cdot}H_2O$ complex which then decays to SiF_3OH and H_2O:

$$H_2O + SiF_4{\cdot}H_2O \rightarrow [TS1] \rightarrow SiF_3OH{\cdot}HF + H_2O \rightarrow SiF_3OH + HF + H_2O$$

Then the SiF_3OH molecule can react either with H_2O forming dihydroxy derivatives:

$$SiF_3OH + H_2O \rightarrow SiF_3OH{\cdot}H_2O \rightarrow [TS2] \rightarrow SiF_2(OH)_2{\cdot}HF \rightarrow SiF_2(OH)_2 + HF$$

or with another SiF_4 molecule forming the siloxane,

$$SiF_3OH + SiF_4 \rightarrow SiF_4{\cdot}SiF_3OH \rightarrow [TS3] \rightarrow SiF_3{-}O{-}SiF_3 + HF$$

Moreover, complexes **II** and **III** can also undergo hydrolysis. At low water concentration in the gas phase, the hydrolysis of complex **II** is the most probable reaction path:

$$2SiF_4{\cdot}H_2O \rightarrow [TS4] \rightarrow SiF_4{\cdot}SiF_3OH{\cdot}HF \rightarrow SiF_4{\cdot}SiF_3OH + HF + H_2O \rightarrow SiF_4 + SiF_3OH + HF + H_2O$$

The geometries of all the structures presented in the scheme above have been optimized at the RHF/6-311G(d,p), MP2/6-311G(d,p), and B3LYP/6-311G(d,p) levels and characterized by vibrational frequency calculations.

We studied 4 elementary steps with nonzero activation energies at the RHF and MP2 levels. These states are designated as TS1−TS4. The transition states have been optimized and characterized by the Hessian calculation. All of these structures have a single imaginary frequency in the infrared spectrum at the both RHF and MP2 levels of theory. The MP2-optimized structures of TS1−TS4 are presented in Figure 2.

The activation energy of the first common step (hydrolysis of first Si−F bond) estimated at the MP2/6-311G(d,p) level is 21 kcal/mol. The transition state TS1 of the reaction is a four-member cyclic structure (see Figure 2a). The single imaginary frequency is 972i cm^{-1} at MP2/6-311G(d,p) (1528i cm^{-1} at RHF/6-311G(d,p)).

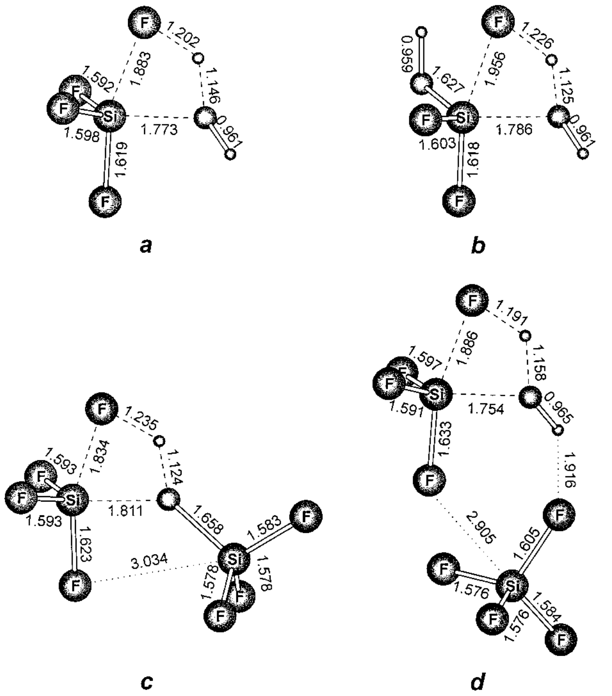

Figure 2. MP2/6-311G(d,p)-calculated structures of transition states TS1−TS4.

The hydrolysis of the second Si−F bond resulting in $SiF_2(OH)_2$ has a slightly higher activation energy of 23 kcal/mol. The corresponding transition state is rather similar to TS1 (see Figure 2b). It should be noted that we located a single TS2 transition state structure having a single imaginary frequency 848i cm^{-1} at MP2/6-311G(d,p) (1347i cm^{-1} at RHF/6-311G-(d,p)) although one can propose two different conformations of the complex $SiF_3OH{\cdot}H_2O$ distinguished by the position of the Si−OH group. In the initial complex, the Si−OH group is additionally coordinated to the oxygen atom of the water molecule and this conformation is the most stable structure of the complex. However, we failed to locate the TS2 structure with the coordinated Si−OH group. During the activation process this group is rotated round the water molecule forming a weak H-bond to the one of fluorine atoms. Thus, the coordination capacity of the oxygen atom of the water molecule is not sufficient to form a four-coordinate state of the oxygen in the activated complex. As will be shown below, a similar situation occurs for another transition state, TS4.

It is interesting that formation of the product ($SiF_3{-}O{-}SiF_3$) is characterized by an activation energy of 30 kcal/mol. The corresponding transition structure, TS3, is shown in Figure 2c. This is a four-member cyclic transition state similar to TS1 with a three-coordinate oxygen atom. The energy of this structure is the largest one among all the transition states considered here. Thus, the most thermodynamically preferred reaction path is simultaneously characterized by the highest activation energy. One can conclude that under nonequilibrium conditions we will observe more hydroxy derivatives in the mixture of SiF_4 and H_2O because the reactions leading to SiF_3OH and $SiF_2(OH)_2$ formation may be faster than the formation of siloxane.

The process of Si−F bond hydrolysis inside complex **II** is characterized by an activation energy of only 13 kcal/mol. This is the smallest activation energy among the reactions under consideration. The corresponding transition state structure, TS4, is shown in Figure 2d. The corresponding single imaginary frequency is 900i cm^{-1} at MP2/6-311G(d,p) (1463i cm^{-1} at RHF/6-311G(d,p)). The structure of this transition state is just the TS1 structure with a second SiF_4 molecule coordinated to the complex by a H-bond (1.92 Å) and a weak additional Si···F coordinate bond (2.91 Å). This additional coordination results in a significant decrease in activation energy in comparison with TS1.

It is intuitively expected that the transition structure resulting from complex **II** should be similar to its structure; i.e., it is expected that TS4 should have Si−O−Si fragment with a four-coordinate oxygen. It should be noted that a preliminary PM3 calculation gave this expected structure. However, we failed to find a structure of this type for TS4 with a four-coordinate oxygen both at the RHF and MP2 levels even when we started from the PM3-optimized structure. The located transition complex has an imaginary frequency 1563i cm^{-1} (RHF/6-311G-(d,p)) corresponding to the O−H−F asymmetric stretch resulting in HF elimination. [It should be noted that we failed to eliminate another imaginary frequency 25i cm^{-1} in this structure. This vibration corresponds to the moving of the whole second coordinated SiF_4 molecule relative to the activated complex $H_2O{\cdot}SiF_4$ and probably has only small effect on the transition structure.] Thus, the oxygen atom, like in TS2, does not have enough coordination capacity to form a fourth coordinate bond in the activated complex TS4. One may reach the conclusion that the energy of activation is higher than the energy of the fourth coordinate bond of oxygen atom or, from another side, the energy difference between the four- and three-coordinated valence states of the oxygen is less than the estimated value of the activation energy, 13 kcal/mol. One can propose that this conclusion is a common rule for the chemistry of inorganic oxygen derivatives.

Conclusion

In the first step of the SiF_4 hydrolysis process, the complex $SiF_4{\cdot}H_2O$ is formed. The most accurate estimate of the binding energy is 2.7 kcal/mol. The calculated vibrational frequencies of the complex $SiF_4{\cdot}H_2O$ are in agreement with experimental infrared bands of the argon matrix-isolated SiF_4/H_2O adduct and allow assigning the observed infrared bands. The s,p-orbitals of silicon play a crucial role in complex formation whereas the d-orbitals have only small effect.

The complexes $SiF_4{\cdot}H_2O$ and $2SiF_4{\cdot}H_2O$ exist in a single conformation whereas the complex $SiF_4{\cdot}2H_2O$ exists in two conformations distinguished by the positions of water molecules. The conformation with the water molecules in positions cis to one another is more energetically favorable. This complex is characterized by electron transfer from the water molecule to the silicon tetrafluoride. The d-orbitals of silicon play a crucial role in the coordinate bond formation of $SiF_4{\cdot}2H_2O$.

The activation energy for the hydrolysis of the first Si−F bond in the complex $SiF_4{\cdot}H_2O$ leading to SiF_3OH is 21 kcal/mol. The quantum-chemical calculations support the conclusion that most stable product in the first steps of hydrolysis is a siloxane $SiF_3{-}O{-}SiF_3$ and that the main direction of the hydrolysis is siloxane formation instead the formation of the polyhydroxy derivatives. However, siloxane formation has the highest activation energy among those considered. The activation energy of the siloxane formation is 30 kcal/mol. Formation of polyhydroxy derivatives is faster but with a less thermodynamically preferred reaction path.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (RFBR Grant Nos. 96-03-32428 and 96-03-33906), International Center for Advanced Studies in Nizhny Novgorod (Grant No. 98-3-02), and Norwegian

Research Council (Project 115883/410). The Gaussian94 program package has been made available by the RFBR (RFBR Grant No 98-07-90290).

References and Notes

(1) Helmbolt, V. O.; Ennan, A. A. *Koord. Khim.* **1983**, *9*, 579.

(2) Sommer, L. *Stereochemistry and Mechanisms of Organosilicon Reactions*; Mir: Moscow, 1966; p 25.

(3) Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.

(4) Ault, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5742.

(5) Reents, W. D., Jr.; Wood, D. L.; Mujsce, A. M. *Anal. Chem.* **1985**, *57*, 104−109.

(6) Sennikov, P. G.; Ikrin, M. A.; Ignatov, S. K.; Bagatur'yants, A. A.; Klimov, E. Yu. *Izv. Akad. Nauk, Ser. Khim.* **1999**, *N1*, in press.

(7) Devyatykh, G. G.; Sennikov, P. G. *Usp. Khim.* **1995**, *64* (9), 817.

(8) Sviderskii, M. F.; Khorozova, O. D.; Dovganich, G. I.; Ivanova, V. A. *Vysokochist. Veshchestva* **1994**, *N1*, 130.

(9) Kleboth, K. *Monatsh. Chem.* **1969**, *100*, 1057.

(10) Plakhotnik, V. N. *Zh. Fiz. Khim.* **1974**, *48*, 2809.

(11) Hu, J.; Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1463.

(12) Marsden, C. J. *Inorg. Chem.* **1983**, *22*, 3177.

(13) Trucks, G. W.; Raghavachari, K.; Higashi, G. S.; Chabal Y. J. *Phys. Rev. Lett.* **1990**, *65*, 504.

(14) Nakasaki, Y.; Miyajima, H.; Katsumata, R.; Hayasaka, N. *Jpn. J. Appl. Phys.* **1997**, *36*, 2533.

(15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.: Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.1*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(17) Evans, D. G.; Yeo, G. A.; Ford, T. A. *Faraday Discuss. Chem. Soc.* **1988**, *86*, 55.

(18) Sverdlov, L. N.; Kovner, M. A.; Krainov, E. V. *Vibrational Spectra of Many-Atom Molecules*; Nauka: Moscow, 1970.

(19) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. R.; McDonald; R. A.; Syverud A. N. *JANAF Thermochemical Tables*, 3rd ed. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(20) Herzberg, G. *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand: NewYork, 1966.