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Thermodynamic and kinetic parameters of elementary steps in gas-phase hydrolysis of SiF_4. Quantum-chemical and FTIR spectroscopic studies

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The energies and thermodynamic parameters of elementary steps in the proposed mechanism of silicon tetrafluoride hydrolysis in the gas phase were calculated by the *ab initio* quantum-chemical method (MP4//MP2/6-311G(2d,2p)) and the density functional theory (B3LYP/6-311G(2d,2p)). The proposed mechanism of gas-phase hydrolysis involves the formation of mono- and dihydroxy derivatives, hexafluorodisiloxane (SiF_3OSiF_3), and linear and cyclic siloxane polymers with the chain length from three to six Si—O and difluorosilanone units. According to the calculations, all reactions considered are endothermic and are characterized by positive Gibbs free energies. The initial hydrolysis steps can be presented with a high accuracy by two parallel processes: formation of trifluorohydroxysilane (SiF_3OH) and SiF_3OSiF_3. These are the most thermodynamically favorable among all reaction channels. The transition states of these elementary steps were found and their kinetic parameters were estimated ($\Delta G^{\neq}$ = 132 and 147 kJ mol^{-1}, respectively). The calculation results were verified using FTIR spectroscopy of a mixture of gas-phase SiF_4 and water vapor. The comparison of the theoretical (absolute) intensities of bands in the IR spectra and integral absorption coefficients in the experimental IR spectrum made it possible to calculate the equilibrium concentrations of the reactants and equilibrium constants of elementary steps of formation of SiF_3OH and SiF_3OSiF_3, which agree with the theoretical values. The role of different derivatives in deep hydrolysis and possibilities of experimental detection of particular intermediates in the gas phase were discussed.

Key words: silicon tetrafluoride, hydrolysis, *ab initio* quantum-chemical calculations, density functional theory, FTIR spectroscopy, trifluorohydroxysilane, hexafluorodisiloxane.

Gaseous silicon tetrafluoride SiF_4 is widely used in modern technologies for the preparation of high-purity silicon, including monoisotopic silicon, and in processes producing fiber light guides.[1] Uncontrolled contact with moisture traces at all stages of synthesis and processing of SiF_4 results in the appearance of numerous oxygen- and hydrogen-containing products of incomplete hydrolysis, which are very difficult to remove.

Hydrolysis of SiF_4 exemplifies a chemical process with a multistage branched mechanism. The full scheme of this process can be written in the simple form

$$SiF_4 + 2\,H_2O \longrightarrow SiO_2 + 4\,HF. \qquad (1)$$

However, it usually occurs incompletely in the gas phase, and intermediate stages involve many parallel reactions to form products and intermediates with different structures and molecular weights. Since these compounds have chemically much in common with each other and with the starting compound, they are difficult to isolate in the individual state or to identify in the reaction mixture. Evidently, the hydrolysis mechanism proposed for the liquid phase,[2] which involves hexacoordinated silicon complex ions and hydroxonium ions, is improbable in the gas phase. In turn, experimental data on this mechanism are fragmentary, and kinetic studies of the total process in the gas phase are rare. It is known that SiF_4 is much more stable toward hydrolysis than other silicon halides. According to the IR spectroscopic[3] and mass spectrometric data,[4] hexafluorodisiloxane SiF_3—O—SiF_3 and, probably, siloxanes with more complicated structures are main admixtures in SiF_4. It was found[5] that dark amorphous precipitates with unidentified (perhaps, polymeric) structures and variable compositions were slowly formed in closed vessels with wet SiF_4. The study of the IR spectrum of SiF_4 showed[6] that the broad nonstructured band at 3760 cm^{-1}, which was mistakenly assigned[7] to the absorption of an HF admixture, was related, in fact, to the formation of silicon hydroxy derivatives (in particular,

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SiF_3OH) upon contact of SiF_4 with moisture. Mass spectroscopic study[4] of pure SiF_4 allowed one to identify ions of the $Si_nF_mH^+$ type and the $F_2Si=O$ fragments. However, it is not clear what molecules are the precursors of these compounds and what is their content in the gas phase. The authors[8] attempted to distinguish particular elementary steps of the gas-phase hydrolysis of SiF_4 using quantum-chemical methods. In particular, the kinetic parameters of hydrolysis of the Si—F bonds in the SiF_4 molecule affording the polyhydroxy derivatives and the thermodynamic parameters of complex formation in the SiF_4—H_2O system and some steps of reaction (1) were determined. Nevertheless, the problem of description of this branched multistep process is far from being solved.

This work is devoted to the study of elementary steps of the incomplete hydrolysis of SiF_4 in the gas phase using quantum-chemical methods and high-resolution FTIR spectroscopy. The purpose is to estimate the thermodynamic and kinetic parameters of the assumed steps of the process and to compare them with available experimental data. A particular problem is the calculation of vibration frequencies and absolute intensities of absorption of probable products of incomplete hydrolysis, which is necessary for the experimental determination of these components in the gas phase from the IR spectra. The IR spectra of a mixture of gaseous SiF_4 with water vapors were studied in the framework of the experimental part of the work. Since these data were obtained for one ratio of partial pressures of the components without variation of the composition and temperature of the mixture, they should be considered as preliminary. The results of the detailed study of the changes in the IR spectrum at different partial pressures of the components and other parameters, as well as assignment of IR absorption bands, will be published elsewhere.

In this work, we restrict our consideration only by the molecular mechanism of hydrolysis. We do not either consider the problems of nucleation and formation of the solid phase, analyzing thus only the initial steps of the hydrolytic process.

Experimental

The molecular geometry was optimized using the density functional theory (B3LYP) and *ab initio* method (MP2) in the 6-311G(2d,2p) basis set. The 6-311G(d,p) basis set was used for the most heavy polymeric compounds. The CBS-QB3 [9] and G2MP2 [10] *ab initio* extrapolation schemes were applied for the description of the thermodynamics of small molecules. In the case of large molecules where extrapolation methods cannot be used, the thermodynamic parameters were calculated from the B3LYP/6-311G(2d,2p) energies and frequencies refining the parameters of the most important elementary steps from the MP4//MP2/6-311G(2d,2p) energy. All quantum-chemical calculations were carried out using the GAUSSIAN-94 [11] and PC GAMESS [12,13] programs.

Silicon terafluoride was prepared by the thermal decomposition of Na_2SiF_6 and purified by low-temperature rectification at the Laboratory of Special-Purity Substances in the Institute of High-Purity Substances (IHPS RAS). IR spectra of the starting SiF_4 (rectificate and its mixture with water) were recorded consecutively in a cell with the 20-cm optical path length, which was placed in the permanently evacuated cell compartment of a Bruker IFS-120HR spectrometer (residual pressure $p = 5 \cdot 10^{-2}$ Torr). To prepare the gas mixture, the specially designed inlet system, which was evacuated to a residual pressure of $5 \cdot 10^{-4}$ Torr, was used. The IR spectrum of the starting SiF_4 (p = 600 Torr) was preliminarily recorded. After the system was evacuated, water vapors were admitted to the cell (p = 5 Torr, an MKS Baratron 722A pressure sensor, accuracy 0.5%), and their spectrum was detected. Then SiF_4 was introduced into the cell (p = 600 Torr), and the spectrum of the mixture was recorded. In quantitative treatment of the spectra, the integral absorption coefficients (IAC) of vibrational-rotational lines in the IR spectra of the H_2O and HF molecules from the HITRAN database[14] were used, and the values calculated in this work were used for the Si_2F_6O and SiF_3OH molecules.

Results and Discussion

Thermodynamic and kinetic parameters of elementary reactions. Based on the available experimental data,[3,6] we can assume that the mechanism of SiF_4 hydrolysis in the gas phase includes the formation of mono-, di-, and polyhydroxy derivatives through the transition states TS1—TS4

$$SiF_4 + H_2O \longrightarrow [TS1] \longrightarrow SiF_3OH + HF, \quad (2a)$$

$$SiF_3OH + H_2O \longrightarrow [TS2] \longrightarrow SiF_2(OH)_2 + HF, \quad (2b)$$

$$SiF_2(OH)_2 + H_2O \longrightarrow [TS3] \longrightarrow SiF(OH)_3 + HF, \quad (2c)$$

$$SiF(OH)_3 + H_2O \longrightarrow [TS4] \longrightarrow Si(OH)_4 + HF. \quad (2d)$$

The monohydroxy derivatives can react with SiF_4 or can be dimerized to form hexafluorodisiloxane

$$SiF_3OH + SiF_4 \longrightarrow [TS5] \longrightarrow SiF_3OSiF_3 + HF, \quad (3a)$$

$$2\,SiF_3OH \longrightarrow [TS6] \longrightarrow SiF_3OSiF_3 + H_2O. \quad (3b)$$

Taking into account the mass spectrometric data that the mixture contains difluorosilanone $F_2Si=O$, we have to supplement the assumed mechanism of hydrolysis by the steps of its formation in the reactions

$$SiF_3OH \longrightarrow [TS7] \longrightarrow F_2Si{=}O + HF, \quad (4a)$$

$$SiF_2(OH)_2 \longrightarrow [TS8] \longrightarrow F_2Si{=}O + H_2O. \quad (4b)$$

Since the hydrolysis of SiF_4 is accompanied presumably by the precipitation of polymers, one has to take into account that linear and cyclic polysiloxanes can be formed

$$n\,SiF_4 + n\,H_2O \longrightarrow \underset{\text{(linear polymer)}}{F(\text{—}SiF_2\text{—}O\text{—})_nH} + (2n - 1)HF, \quad (5a)$$

$$n\,SiF_4 + n\,H_2O \longrightarrow \underset{\text{(cyclic polymer)}}{(\text{—}SiF_2\text{—}O\text{—})_n} + 2n\,HF. \quad (5b)$$

The detailed mechanism of condensation reactions (5) can be presented by the sequence of reactions (2) and (3).

It is also evident that branched polymers can be formed during hydrolysis, and this process is described by the combination of Eqs. (5a) and (5b).

The optimized geometric parameters and total energies of the main participants of reactions (2)—(5) are presented in Table 1. The thermodynamic parameters of these steps calculated per mole of the starting SiF_4 are presented in Table 2.

It follows from the data in Table 2 that all considered steps of hydrolysis are endothermic and are characterized by positive Gibbs free energies. This can explain, most likely, the sufficiently high stability of SiF_4 toward moisture, because the equilibrium of all elementary steps is shifted toward the starting reactants, at least to solid phase formation.

From the thermodynamic point of view, among all processes considered, the formation of difluorosilane ($F_2Si{=}O$) is the least favorable process. Like the enthalpy, the Gibbs free energy of this reaction is much higher (by 200—400 kJ mol^{-1}) than the corresponding parameters of other elementary processes. It should be noted that this result was obtained by different quantum-chemical methods and, in addition, agrees with the result of calculation of $\Delta_f G(SiF_2O)$ from the experimental IR frequencies of this compound in an inert low-temperature matrix.[15] Thus, it can be asserted that the formation of the silanone derivatives under the equilibrium gas-phase conditions is improbable at standard temperatures. The peak of $SiF_2{=}O$ is observed in the mass spectrum likely due to the appearance of this compound under nonequilibrium conditions during the ionization of samples in the instrument or due to the decomposition of some hydrolysis products adsorbed on the walls of the ionization chamber.

The cyclic polymeric hydrolysis products are less thermodynamically favorable than the linear polymers. However, as the size of the cycle is enlarged, the energy, enthalpy, and Gibbs free energy of these products decrease monotonically and at n = 4—6 become comparable with the corresponding parameters of the linear polymers. This suggests that the linear polymers are formed at the initial stages of hydrolysis. The chains grow to n = 4—6, after which their molecules begin to form cycles. This fact is of

Table 1. Total energies (E_{tot}/au) and geometric parameters (bond lengths in Å, angles in deg) calculated by different methods for the molecules mainly involved in reactions (2)—(5)

Molecule (symmetry)	Parameter		B3LYP/6-311G(2d,2p)	MP2/6-311G(2d,2p)
SiF_4 (T_d)	E_{tot}		−689.291227	−688.127781
	Bond	Si—F	1.568	1.566
H_2O (C_{2v})	E_{tot}		−76.452117	−76.289212
	Bond	O—H	0.961	0.957
	Angle	H—O—H	104.1	103.2
HF ($C_{\infty v}$)	E_{tot}		−100.473572	−100.297095
	Bond	H—F	0.921	0.915
SiF_3OH (C_s)	E_{tot}		−665.256290	−664.107711
	Bond	Si—F	1.571, 1.578	1.569, 1.576
		Si—O	1.609	1.609
		O—H	0.958	0.955
	Angle	Si—O—H	119.8	119.6
$SiF_2(OH)_2$ (C_2)	E_{tot}		−641.219850	−640.085912
	Bond	Si—F	1.589	1.579
		Si—O	1.614	1.621
		O—H	0.958	0.956
	Angle	F—Si—F	105.1	108.6
		O—Si—O	107.9	115.1
		Si—O—H	118.3	117.8
SiF_3—O—SiF_3 (C_2)	E_{tot}		−1254.057813	−1251.927176
	Bond	Si—F	1.569, 1.570, 1.572	1.568, 1.569, 1.571
		Si—O	1.611	1.610
	Angle	Si—O—Si	145.3	145.4
		O—Si—F	109.0, 110.4, 110.6	109.1, 110.4, 110.5
		F—Si—Si—F*	69.9	68.1
$F_2Si{=}O$ (C_{2v})	E_{tot}		−564.639868	−563.667055
	Bond	Si—F	1.573	1.571
		Si—O	1.504	1.513
	Angle	F—Si—O	127.7	127.7

* Dihedral angle between the F atoms, on the bisecting plane of which the O atom is localized.

Table 2. Energy ($\Delta_r E_{tot}$), standard enthalpy ($\Delta_r H^\circ$), and standard Gibbs free energy ($\Delta_r G^\circ$) (per mole of SiF_4) calculated by the B3LYP/6-311G(2d,2p) method for the hydrolysis of SiF_4

Reaction	$\Delta_r E_{tot}$	$\Delta_r H^\circ(298)$	$\Delta_r G^\circ(298)$
		kJ mol^{-1}	
$SiF_4 + 1/2\ H_2O = 1/2\ SiF_3—O—SiF_3 + HF$	38.9 (31.4)[a]	37.6 (30.1)[a]	32.6 (25.1)[a]
$SiF_4 + H_2O = SiF_3OH + HF$	35.4 (33.6)[a]	33.5 (31.7)[a]	27.0 (26.3)[a]
$SiF_4 + 2/3\ H_2O = 1/3\ SiF_3(OSiF_2)_2F + 4/3\ HF$	52.0	50.3	46.4
$SiF_4 + H_2O = 1/6\ Si_6F_{12}O_6 + 2\ HF$	(51.7)[b]	—	—
$SiF_4 + H_2O = 1/5\ Si_5F_{10}O_5 + 2\ HF$	(52.3)[b]	(48.7)[b]	(42.4)[b]
$SiF_4 + H_2O = 1/4\ Si_4F_8O_4 + 2\ HF$	82.1	75.8	74.2
$SiF_4 + 2\ H_2O = SiF_2(OH)_2 + 2\ HF$	74.7	71.3	67.7
$SiF_4 + H_2O = 1/3\ Si_3F_6O_3 + 2\ HF$	86.7	82.4	73.2
$SiF_4 + H_2O = 1/2\ Si_2F_4O_2 + 2\ HF$	157.0	151.4	134.1
$SiF_4 + H_2O = SiF_2O + 2\ HF$	410.4	400.6 (382.1)[c]	355.3 (337.4)[c]

[a] Calculated from the energy (MP4//MP2/6-311G(2d,2p)) and frequencies (B3LYP/6-311G(2d,2p)).

[b] Calculated by the B3LYP/6-311G(d,p) method.

[c] Calculation by the G2MP2 method.

interest from the viewpoint that structural units of many crystalline modifications of SiO_2 (in particular, cristobalite) can be considered as cross-linked six-membered siloxane cycles.

It is important that the formation of the dihydroxy derivative $SiF_2(OH)_2$ is much less thermodynamically favorable than the formation of SiF_3OH, and the thermodynamic characteristics of this step are comparable with the parameters for small cyclic polymers ($n = 3, 4$). Evidently, the formation of the tri- and tetrahydroxy derivatives is less energetically favorable. This suggests that the di- and polyhydroxy derivatives are not virtually involved in the initial steps of SiF_4 hydrolysis.

Two reactions yielding SiF_3OH and $SiF_3—O—SiF_3$ as products are most energetically favorable from the thermodynamic point of view. Although different calculation methods lead to somewhat contradictory conclusions about their relative favorability, both these reactions are characterized by approximately equal energies, enthalpies, and free Gibbs energies. The latter are much lower (by almost 20 kJ mol^{-1}) than the corresponding value for the closest in energy step of formation of the linear polymers. This conclusion is confirmed by the calculations using both the density functional theory and *ab initio* method. In the case of SiF_3OH, the conclusion is additionally confirmed by the calculation using the CBS-QB3 extrapolation scheme, which gives $\Delta_r G^\circ(298) = 26.4$ kJ mol^{-1} for reaction (2a).

Thus, analysis of the thermodynamic parameters of reactions (2)—(5) suggests that the initial steps of hydrolysis preceding the accumulation of the polymeric products and formation of the solid phase can be presented with a high accuracy as only two parallel processes

$$SiF_4 + H_2O \longrightarrow SiF_3OH + HF, \tag{6a}$$

$$SiF_4 + 1/2\ H_2O \longrightarrow 1/2\ F_3Si—O—SiF_3 + HF. \tag{6b}$$

For the MP4//MP2/6-311G(2d,2p) calculation, reaction (6b) is somewhat more favorable than reaction (6a). The latter is evidently a bimolecular reaction that proceeds through the transition state with a pentacoordinated Si atom and, perhaps, with the formation of a binary prereaction complex, which has previously been observed in the inert low-temperature matrix[16] and studied by the quantum-chemical methods.[8] Reaction (6b) can proceed *via* the mechanism of heterofunctional (3a) and homofunctional condensation (3b). The formation of hexafluorodisiloxane *via* both mechanisms is characterized by the same thermodynamic effect calculated per mole of SiF_4 but the kinetic parameters of the process can differ. In order to determine the latter, we searched for the corresponding transition states TS1, TS5, and TS6. In addition, the transition state TS2 was determined to evaluate the kinetic differences between elementary reactions (2a) and (2b).

The structures and geometric parameters of the TS optimized by the B3LYP/6-311G(2d,2p) method are presented in Fig. 1. The calculated standard kinetic parameters of possible elementary reactions affording SiF_3OH and $SiF_3—O—SiF_3$ and (for comparison) the kinetic parameters of the $SiF_2(OH)_2$ formation are presented in Table 3.

As follows from the data in Table 3, the formation of SiF_3OH (6a) occurs most easily kinetically (with the lowest $\Delta G^{\neq}$), while reaction (6b) prefers mechanism (3b) for which $\Delta G^{\neq}$ is almost 20 kJ mol^{-1} lower than that for reaction (3a). However, it should be taken into account that reaction (3b) has the second order with respect to SiF_3OH, whose concentration can be low compared to that of SiF_4. In this case (at a very low concentration of H_2O), heterofunctional condensation can prevail. The homofunctional mechanism of condensation predominates at a relatively high concentration of H_2O.

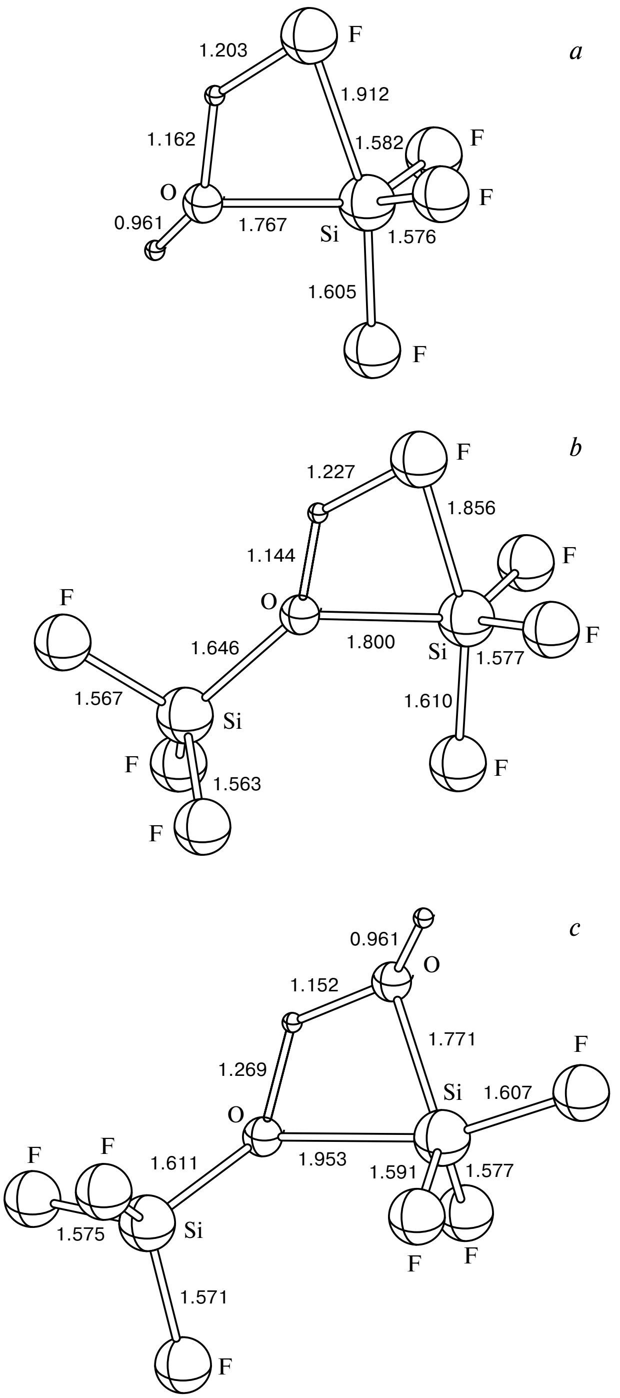

Fig. 1. Structures of transition states of reactions (2a) (*a*), (3a) (*b*), and (3b) (*c*) optimized by the B3LYP/6-311G(2d,2p) method; internuclear distances are given in Å.

For the elementary reaction of $SiF_2(OH)_2$ formation, the $\Delta G^{\neq}$ values are only slightly lower than those for reaction (6a). Thus, the absence of $SiF_2(OH)_2$ and other polyhydroxy derivatives in the equilibrium mixture is explained by the thermodynamic factors only. The kinetic factors can become primary at the polymerization stage because the Gibbs energy of $SiF_2(OH)_2$ formation is comparable with the thermodynamic parameters of formation of the polymers. Thus, the dihydroxy derivatives can appear in deeper steps of hydrolysis to produce branched polymers.

Vibrational frequencies and absolute intensities of bands in the IR spectra of the Si_2F_6O and SiF_3OH molecules. As mentioned above, IR spectroscopy makes it possible to detect admixtures of $SiF_3—O—SiF_3$ and SiF_3OH in SiF_4. At the same time, their quantitative determination requires an information on the integral absorption coefficients (IAC) of bands of the main vibrations in the spectrum. These experimental data are lacking for the molecules under study, and the substances in the individual state are inaccessible, which does not allow these important spectroscopic parameters to be determined. Therefore, the vibrational frequencies and IAC of bands in the IR spectra of the Si_2F_6O and SiF_3OH molecules were calculated in this work.

The geometric parameters, vibrational frequencies, and intensities of bands in the IR spectrum of the SiF_3OH molecule were calculated by the B3LYP/6-311G(2d,2p) and B3LYP/cc-pVQZ methods, which are rather reliable for the estimation of the IR spectroscopic parameters of SiF_4, SiH_4 molecules and mixed fluorosilanes.[17] Both calculated methods result in a methanol-like structure with the C_s symmetry (see Table 1). The assignment of vibrations of this molecule and calculated vibrational frequencies and band intensities in the IR spectrum are presented in Table 4. In order to compare the harmonic frequencies with the experimental values, we used the scaling factor $k = 0.9588$, which was chosen by the comparison of the theoretical and experimental frequencies of the stretching vibration of the OH group in the MeOH molecule.[18] The value 3745 cm^{-1} obtained by scaling is the theoretical estimate of the position of the center of the stretching vibration ν(OH) band in the IR spectrum of SiF_3OH. This allows us to assign the broad absorption band observed in the region of 3725—3800 cm^{-1} with the center at 3762 cm^{-1} to stretching vibrations of the OH group in the SiF_3OH molecules.

The quantum-chemical calculation of the $F_3Si—O—SiF_3$ molecule gives a bent structure (symmetry C_2) with the Si—O—Si angle ~145° (see Table 1). The F atoms of the opposite SiF_3 groups are in the alternating conformation, and the O atom is localized in the bisector plane of the dihedral angle formed by two F atoms of the opposite SiF_3 groups. The B3LYP/6-311G(2d,2p)-calculated vibrational frequencies, intensities of bands in the IR spectrum, and assignment of vibrations of the $F_3Si—O—SiF_3$ molecule are presented in Table 5. As a whole, these data are well consistent with the experimental frequencies of hexafluorodisiloxane.[3,19] Some differences are observed in the assignment of normal vibrations, which were assigned by

Table 3. Total energies of the transition states ($E_{tot}^{\neq}$) and standard kinetic parameters calculated by the B3LYP/6-311G(2d,2p) method for elementary steps of the incomplete hydrolysis of SiF_4

Reaction	$-E_{tot}^{\neq}$ /au	$\Delta E_{tot}^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$
		kJ mol^{-1}		
$SiF_4 + H_2O = SiF_3OH + HF$	765.706624	96.4	91.1	132.5
$2\ SiF_3OH = SiF_3—O—SiF_3 + H_2O$	1330.475188	98.2	93.3	147.5
$SiF_3OH + SiF_4 = SiF_3—O—SiF_3 + HF$	1354.499086	127.1	120.6	166.4
$SiF_3OH + H_2O = SiF_2(OH)_2 + HF$	741.674912	87.9	84.9	136.5

the force field method,[19] probably because the C_{2v} symmetry was used.

The data in Tables 4 and 5 make it possible to estimate the absolute intensities of the most important bands observed in the IR spectra of the SiF_3OH and Si_2F_6O molecules. The absolute intensity of the ν(OH) vibration band of the SiF_3OH molecule calculated by the B3LYP/cc-pVQZ method is 136 km mol^{-1}. The B3LYP/6-311G(2d)-estimated absolute intensity of the band of the antiphase symmetric stretching vibration of two SiF_3 groups (ν_{15}, see Table 5), to which we assign the band at 838 cm^{-1} in the spectrum of Si_2F_6O, is equal to 96 km mol^{-1}. It has previously been shown that the absolute intensities of bands in the IR spectra of SiF_4, SiH_4, and mixed fluorosilanes[17] calculated by similar methods overestimate the results by 20% on the average. Taking into account this correction and reducing the result to one significant digit, one can obtain the following theoretical estimate of the absolute intensities of the above vibrations:

$$A_{3762}(\nu(OH), SiF_3OH) = (110\pm20)\ \text{km mol}^{-1} = \\ = (50\pm10)\cdot10^{-8}\ \text{cm}^2\ \text{s}^{-1}\ \text{molec.}^{-1},$$

$$A_{838}(\nu_{15}, Si_2F_6O) = (80\pm20)\ \text{km mol}^{-1} = \\ = (40\pm10)\cdot10^{-8}\ \text{cm}^2\ \text{s}^{-1}\ \text{molec.}^{-1}$$

The intensity (peak absorption coefficient) of the band at 838 cm^{-1} in the IR spectrum of hexafluorodisiloxane has previously[3] been determined experimentally. However, the error of its determination was not presented. We can attempt to estimate the IAC of this band ($16\cdot10^{-8}$ cm^2 s^{-1} molec.$^{-1}$) from the experimental spectrum.[3] The error of this procedure is very high and, unfortunately, cannot be determined, When restricting ourselves by one significant digit ($20\cdot10^{-8}$ cm^2 s^{-1} molec.$^{-1}$), we obtain the estimate which is twofold lower than the theoretical value ($40\cdot10^{-8}$ cm^2 s^{-1} molec.$^{-1}$). Averaging the experimental and theoretical values, we obtain the estimate

$$A_{838}(\nu_{15}, Si_2F_6O) = (30\pm10)\cdot10^{-8}\ \text{cm}^2\ \text{s}^{-1}\ \text{molec.}^{-1},$$

which will be used in further calculations of the concentration of the hexafluorodisiloxane admixture.

FTIR spectroscopy of a mixture of gaseous SiF_4 with water vapors. The fragments of the IR spectra of the starting SiF_4 (p = 600 Torr) and its mixture with water vapors (p = 5 Torr) in the regions corresponding to the vibrations of HF, stretching vibrations of the OH group, and vibration of the Si_2F_6O molecule (838 cm^{-1}) are presented in Figs. 2—4. It is seen that all indicated participants of hydrolysis are already present in the starting purified SiF_4. When water vapors are added, the intensities of the spec-

Table 4. Vibrational frequencies (ν/cm^{-1}) and absolute intensities of bands (I/km mol^{-1}) in the IR spectrum of the SiF_3OH molecule calculated by the B3LYP/6-311G(2d,2p) and B3LYP/cc-pVQZ methods

Band	Assignment	B3LYP/6-311G(2d,2p)		B3LYP/cc-pVQZ	
		ν	I	ν	I
1	ω(OH around Si—O)	82.4	106.1	137.8	101.3
2	$\rho(SiF_3)$	264.5	1.7	265.3	1.7
3	$\rho(SiF_3)$ + ω(OH around Si—O)	275.3	14.7	276.8	18.5
4	$\delta_{as}(SiF_3)$	364.6	39.6	366.1	37.3
5	$\delta_{as}(SiF_3)$	378.1	44.3	378.2	38.7
6	$\delta_s(SiF_3)$	387.0	49.8	386.7	48.4
7	$\nu_s(SiF_3)$ + ν(Si—O) + δ(H—O—Si)	771.4	11.5	762.7	62.9
8	δ(H—O—Si)	821.8	174.5	796.1	115.0
9	ν_{as}(F—Si—F)	984.4	202.4	974.2	220.6
10	ν(Si—O) + $\nu_{as}(SiF_3)$	1011.3	228.4	1000.5	244.0
11	ν(Si—O) – $\nu_s(SiF_3)$	1043.2	169.8	1030.4	191.3
12	ν(OH)	3911.1	127.9	3901.6	135.7

Table 5. Vibrational frequencies (ν/cm^{-1}), absolute intensities in the IR spectrum (*I*/km mol^{-1}), and assignment of vibrations of the $F_3Si—O—SiF_3$ molecule calculated by the B3LYP/6-311G(2d) method and experimental frequencies of absorption bands of hexafluorodisiloxane in the gas phase

Band	Assignment	Calculation		Experiment[a], ν	
		ν	*I*	I[b]	II[c]
1	$\omega(F_3Si) + \omega(SiF_3)$	12.5	0.1		
2	$\omega(F_3Si) - \omega(SiF_3)$	18.1	0.0		
3	$\delta(Si—O—Si)$	57.2	0.3	85 w	
4	$\rho(F_3Si) + \rho(SiF_3)$	210.0	0.0	179 m	
5	$\rho(F_3Si) - \rho(SiF_3)$	210.8	1.1		
6	$\rho(F_3Si) + \rho(SiF_3)$	231.5	0.9	(227)[d] vw	
7	$\delta_{as}(F_3Si) - \delta_{as}(SiF_3) + \delta(Si—O—Si)$	275.5	3.1		
8	$\delta_{as}(F_3Si) - \delta_{as}(SiF_3)$	306.1	20.2		304 w
9	$\delta_{as}(F_3Si) + \delta_{as}(SiF_3)$	344.4	17.8	(343)[d] vw	375 w
10	$\nu_s(F_3Si) + \nu_s(SiF_3)$	347.1	0.1		388 w
11	$\delta_s(F_3Si) - \delta_s(SiF_3)$	394.3	152.7	402 m	401 s
12	$\rho(F_3Si) - \rho(SiF_3)$	415.9	80.5	434 m/s	432 m/s
13	$\delta(Si—O—Si) + \rho(F_3Si) + \rho(SiF_3)$	442.7	34.7	601 w	595 vw
14	$\delta_s(F_3Si) + \delta_s(SiF_3) + \nu_s(Si—O—Si)$	634.2	21.1	631 m/s	660 vw
15	$\nu_s(F_3Si) - \nu_s(SiF_3)$	822.6	95.7	838 m/s	838 m/s
16	$\nu_s(F_3Si) + \nu_s(SiF_3) + \nu_s(Si—O—Si)$	936.4	33.6	(940)[d] w	912 w
17	$\nu_{as}(F_3Si) - \nu_{as}(SiF_3)$	1005.6	50.3		981 m
18	$\nu_{as}(F_3Si) - \nu_{as}(SiF_3)$	1006.4	12.4		
19	$\nu_{as}(F_3Si) + \nu_{as}(SiF_3)$	1018.5	359.4	989 m	1028 vs
20	$\nu_{as}(F_3Si) + \nu_{as}(SiF_3) + \delta(Si—O—Si)$	1022.3	338.2		
21	$\nu_{as}(Si—O—Si)$	1168.8	692.3	1206 s	1200 vs

[a] W, m, and s are weak, medium, and strong bands, respectively; v is very.

[b] See Ref. 19. Two very weak broadened bands (555 and 453 cm^{-1}) in the experimental spectrum[19] cannot be assigned on the basis of quantum-chemical calculations.

[c] See Ref. 3. The weak bands in the experimental spectrum lying higher than 1200 cm^{-1} (integral frequencies and overtones) are not presented.

[d] The bands detected only in the crystalline state.

tral lines of all substances considered tend to increase, and the lines from the region of stretching vibrations of the excess water molecule predominate in Fig. 3. The experiment showed that the observed intensities of the IR bands remain almost unchanged in time. Thus, the time required for the establishment of equilibrium in the system under study is shorter than the time of spectrum recording, which is ~3 h.

As indicated above, using the results of quantum-chemical calculations, we interpret the broad band with the center at 3762 cm^{-1} (see Fig. 3) as vibrations of the OH groups in molecules of hydroxyl-containing hydrolysis products. Since SiF_3OH prevails among the latter, it can be assumed that the IAC of this band corresponds to the absorption of the SiF_3OH molecule. Using the absolute intensities of lines and bands in the spectra of the HF and H_2O molecules from the HITRAN database and the above values for the silicon-containing components, we can determine the equilibrium concentrations of the reaction participants in the mixture (Table 6) and estimate

Table 6. Experimental integral intensities of the IR bands (*B*/cm^{-1}), equilibrium partial pressures (*p*/Torr), and concentrations (*C* (mol.%)) of the participants of hydrolysis in the starting SiF_4 and its gas-phase mixture with H_2O

Compound	Maximum of band, ν/cm^{-1}	Starting SiF_4 (600 Torr)			Mixture SiF_4 (600 Torr) + H_2O (5 Torr)		
		B	*p*	*C*	*B*	*p*	*C*
Si_2F_6O	838	6.8	1	0.15	11.5	1.8	0.3
SiF_3OH	3762	0.1	0.01	$2 \cdot 10^{-3}$	5.8	0.5	0.08
H_2O	—*	0.002	0.01	$2 \cdot 10^{-3}$	0.28	2.1	0.35
HF	—*	0.004	0.003	$5 \cdot 10^{-4}$	0.12	0.08	0.01

* The resolved lines of the rotational-vibrational spectrum from the HITRAN database were used.[14]

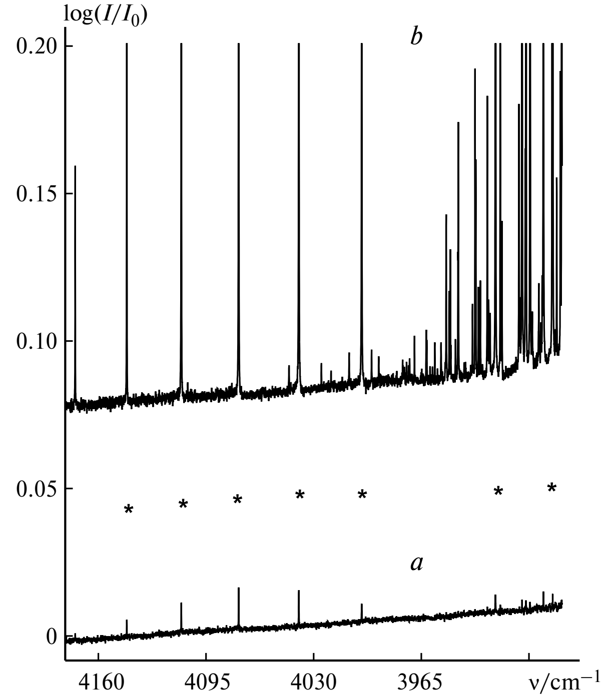

Fig. 2. Region of the IR absorption spectrum at 4180—3880 cm^{-1} containing the absorption lines of HF (marked by asterisk) and water (others) (l = 20 cm, resolution 0.05 cm^{-1}): (*a*) SiF_4-rectificate (p = 600 Torr) and (*b*) SiF_4-rectificate (p = 600 Torr) + H_2O (p = 5 Torr).

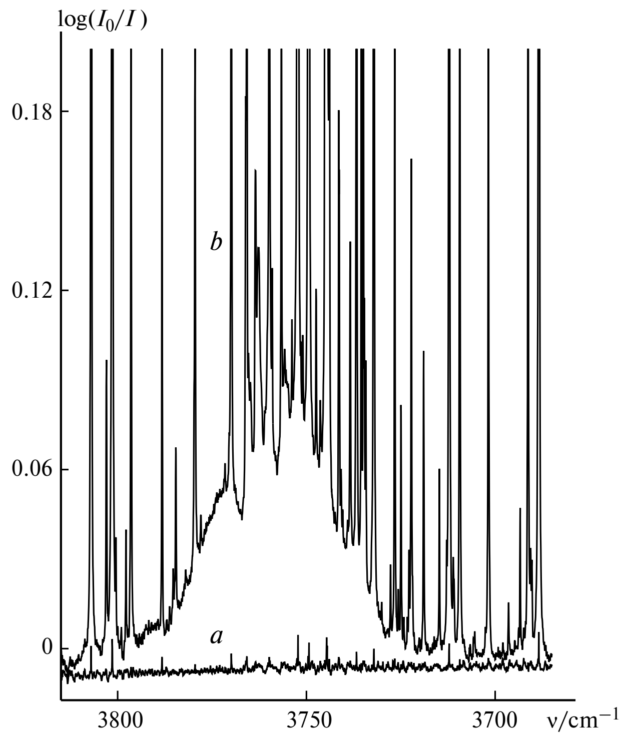

Fig. 3. Region of the IR absorption spectrum at 3825—3675 cm^{-1} containing the absorption band of SiF_3OH (l = 20 cm, resolution 0.05 cm^{-1}): (*a*) SiF_4-rectificate (p = 600 Torr) and (*b*) SiF_4-rectificate (p = 600 Torr) + H_2O (p = 5 Torr).

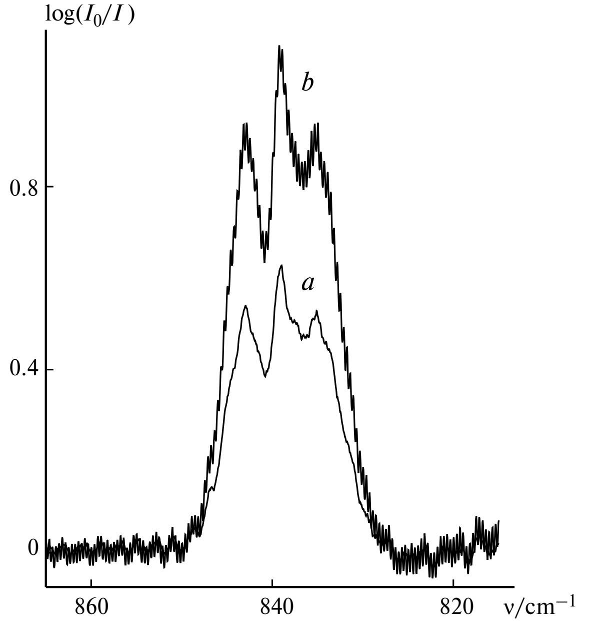

Fig. 4. Region of the IR absorption spectrum at 865—815 cm^{-1} containing the absorption band of Si_2F_6O (l = 20 cm, resolution 0.05 cm^{-1}): (*a*) SiF_4-rectificate (p = 600 Torr) and (*b*) SiF_4-rectificate (p = 600 Torr) + H_2O (p = 5 Torr).

the experimental equilibrium constants K_{p1} and K_{p2} and Gibbs energies ΔG_{r1} and ΔG_{r2} for reactions (2a) and (3), respectively.

$$K_{p1} = \frac{[SiF_3OH][HF]}{[SiF_4][H_2O]} = 3.2 \cdot 10^{-5},$$

$$\Delta G_{r1} = -RT\ln K_{p1} = 25.7 \text{ kJ mol}^{-1};$$

$$K_{p1} = \frac{[Si_2F_6O]^{1/2}[HF]}{[SiF_4][H_2O]^{1/2}} = 12.4 \cdot 10^{-5},$$

$$\Delta G_{r2} = -RT\ln K_{p2} = 22.3 \text{ kJ mol}^{-1}.$$

The calculation of K_{p1} and K_{p2} from the theoretical ΔG_r (ΔG_r^{calc}) values gives the result that agrees with the experimental values

$$K_{p1} = \exp(-\Delta G_{r1}/RT) = 2.5 \cdot 10^{-5}$$

$$(\Delta G_{r1}^{calc} = 26.3 \text{ kJ mol}^{-1}),$$

$$K_{p2} = \exp(-\Delta G_{r2}/RT) = 4.0 \cdot 10^{-5}$$

$$(\Delta G_{r1}^{calc} = 25.1 \text{ kJ mol}^{-1}).$$

Thus, the quantum-chemical calculation of the thermodynamic parameters of the elementary steps of hydrolysis (see Table 2) and assumption that the hydrolysis proceeds at the initial steps as a combination of reactions (6a) and (6b) agree well with the experimental data.

It is of interest that the calculation of the equilibrium concentrations from the estimated K_{p1} and K_{p2} values gives the results, which are far from the experimental values in the case of both theoretical and experimental equilibrium constants. The equilibrium partial pressures (p/Torr) calculated for various molecules from the theoretical (I) and experimental equilibrium constants (II) are presented below.

Molecule	p^{I}	p^{II}
H_2O	4.66	4.51
HF	0.54	0.87
SiF_3OH	0.13	0.10
Si_2F_6O	0.21	0.39

Comparison with the data in Table 6 shows that the calculation overestimates almost twofold the equilibrium concentration of H_2O, and the HF concentration is overestimated by almost 10 times. At the same time, the equilibrium concentrations of SiF_3OH and Si_2F_6O are underestimated.

This divergence can be explained, most likely, by the fact that heterophase processes (for example, adsorption on the walls and the reaction of HF with the metallic part of the equipment), which remove H_2O and HF from the gas phase, occur in the spectroscopic cell and the inlet system of the IR spectrometer. Since the equilibrium constant in the gas phase remains unchanged (and agrees with the theoretical value), this results in the shift of equilibrium toward the formation of SiF_3OH and $SiF_3—O—SiF_3$. As can be seen from the data in Table 6, considerable amounts of H_2O and HF are removed from the equilibrium mixture, resulting in exceeding the theoretical concentrations over the observed values.

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References

1. G. G. Devyatykh, A. D. Bulanov, A. V. Gusev, P. G. Sennikov, and A. M. Prokhorov, E. M. Dianov, Kh.-I. Pol´, *Dokl. Akad. Nauk*, 2001, **376**, 492 [*Dokl. Chem.*, 2001 (Engl. Transl.)].
2. V. O. Gel´mbol´dt and A. A. Ennan, *Koord. Khim.*, 1983, **9**, 579 [*Russ. J. Coord. Chem.*, 1983, **9** (Engl. Transl.)].
3. W. D. Reents, Jr., D. L. Wood, and A. M. Muscle, *Anal. Chem.*, 1965, **57**, 104.
4. G. G. Devyatykh, D. A. Pryakhin, and A. D. Bulanov, *Neorgan. Materialy*, 2001, **37**, 498 [*Inorg. Mater.*, 2001, **37** (Engl. Transl.)].
5. A. V. Loginov and A. M. Garbar, *Vysokochist. Veshchestva* [*High-Purity Substances*], 1989, No. 5, 27 (in Russian).
6. P. G. Sennikov, M. A. Ikrin, S. K. Ignatov, A. A. Bagatur´yants, and E. Yu. Klimov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 92 [*Russ. Chem. Bull.*, 1999, **48**, 93 (Engl. Transl.)].
7. M. F. Sviderskii, O. D. Khorozova, G. I. Dovganich, and V. A. Ivanova, *Vysokochist. Veshchestva* [*High-Purity Substances*], 1994, No. 1, 130 (in Russian).
8. S. K. Ignatov, P. G. Sennikov, B. S. Ault, A. A. Bagatur´yants, A. A. Simdyanov, A. G. Razuvaev, E. Yu. Klimov, and O. Gropen, *J. Phys. Chem.*, *A*, 1999, **103 (41)**, 8328.
9. J. A. Montgomery, M. J. Frisch, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.*, 1999, **110**, 2822.
10. L. A. Curtiss, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.*, 1993, **98**, 1293.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94*, *Revision D.1*, Gaussian, Inc., Pittsburgh (PA), 1995.
12. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
13. PC GAMESS home page: http://classic.chem.msu.su/gran/gamess/index.html.
14. L. S. Rothman, C. P. Rinsland, A. Goldman, S. T. Massie, D. P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCannn, R. P. Gamache, R. B. Wattson, K. Yoshino, K. V. Chance, K. W. Jucks, L. R. Brown, V. Nemtchinov, and P. Varanasi, *J. Quant. Spectrosc. Radiat. Transfer*, 1998, **60**, 667.
15. M. W. Chase, *J. Phys. Chem. Ref. Data*, 1998, **9**, 1.
16. B. S. Ault, *J. Am. Chem. Soc.*, 1983, **105**, 5742.
17. S. K. Ignatov, P. G. Sennikov, A. G. Razuvaev, and K. G. Tokhadze, *Opt. Spektroskop.*, 2001, **90**, 654 [*Opt. Spectroscopy*, 2001, **90** (Engl. Transl.)].
18. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, Consolidated Volume I, National Bureau of Standards, Washington (DC), 1972.
19. J. R. Durig, V. F. Kalasinsky, and M. J. Flanagan, *Inorg. Chem.*, 1975, **14**, 2839.

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