Hydrolysis of tetrafluorosilane under neutral conditions: a quantum chemical study

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A density functional quantum chemical study of the first step of SiF_4 hydrolysis under neutral conditions in the presence of one or two H_2O molecules was carried out. The reaction is endothermic and can follow three different pathways that involve the formation of pentacoordinated (pathway *A*) and hexacoordinated (pathways *B* and *C*) intermediates and transition states as the key steps. Pathway *B* is the most energetically favorable. All three pathways of the hydrolysis reaction lead to a product with formal retention of the configuration of substituents at the silicon atom.

Key words: hydrolysis, silanes, nucleophilic substitution, quantum-chemical calculations, density functional theory, transition states.

Hydrolysis of halosilanes is one of the most important reactions in industrial chemistry of organoelement compounds. Products obtained using this process, namely, siloxanes and polysesquiloxanes, are widely used in various fields of science and technology.[1—5] The hydrolysis reaction is a nucleophilic substitution reaction. Nucleophilic substitution at silicon atom has been comprehensively studied by various experimental methods.[6,7] The results obtained in a large number of theoretical studies of nucleophilic substitution at Si atom under the action of anions (H^-, Hal^-, *etc.*) are available.[8—14] Literature on the reactions involving neutral molecules as nucleophiles is somewhat less extensive.[15—20] The aim of this work was to carry out a density functional study of the first step of SiF_4 hydrolysis. This substrate, tetrafluorosilane, has a relatively simple structure and comprehensive treatment of its reactions can favor elucidation of all possible channels of the hydrolysis of halosilanes.

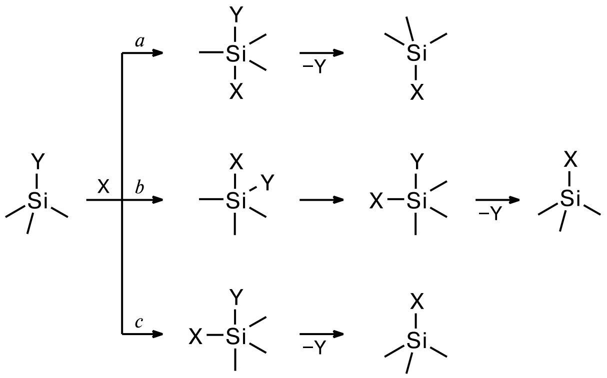
Calculation Procedure

Our density functional (DFT) study was carried out using the *ab initio* generalized gradient approximation and the PBE functional[21,22] with the TZ2P basis set and the PRIRODA program.[23] Geometry optimization was carried out for all stable compounds and for the structures corresponding to the saddle points (in the case of transition states, TS). The types of the stationary points were confirmed by the vibrational frequency analysis. For the saddle points, the reaction coordinates were also calculated.

Results and Discussion

Based on the results of analysis of experimental data on the reactions of nucleophilic substitution at silicon atom, three possible mechanisms of the process under study were formulated (Scheme 1).[7]

Scheme 1



Route *a* leads to a product with inverted configuration of substituents at the silicon center while routes *b* and *c* lead to a compound with retention of the configuration at the silicon atom (due to pseudorotation according to Berry in the case of route *b*). Analysis of reaction products showed that the feasibility of a particular mechanism and, hence, the stereochemistry of the process depends on the nature of the substrate, nucleophile, and the solvent. The

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key step of the mechanisms *a—c* is the formation of a species containing a pentacoordinate Si atom. However, there are numerous experimental data that confirm the existence of hexacoordinate silicon compounds, especially in the presence of more than one electron-acceptor substituent at the silicon atom.[24] In particular, the existence of various pentafluorosilicates $[SiF_5(H_2O)]^-$ in aqueous solutions and the formation of $SiF_4(H_2O)_2$ upon dissolution of SiO_2 in aqueous H_2SiF_6 solution was proved.[24] A quantum chemical study of the system SiF_4—H_2O at low water concentrations showed that complex $SiF_4(H_2O)$ corresponds to a minimum on the potential energy surface (PES).[25] This was confirmed by IR spectroscopy.[25] According to B3LYP and MP2 calculations, minima on the PES of the tetrafluorosilane—water system correspond not ony to the $SiF_4(H_2O)$ complex but also to the species $(SiF_4)_2(H_2O)$, *cis*-$SiF_4(H_2O)_2$, and *trans*-$SiF_4(H_2O)_2$, the *cis*-isomer being thermodynammically more favorable than the *trans*-isomer. Therefore, hydrolysis of tri- or tetrahalogensilanes can proceed not only *via* pentacoordinate but also hexacoordinate transition states.

A number of quantum chemical studies of the hydrolysis reactions of various silanes under neutral conditions were reported.[15—19] In particular, three steps of trichlorosilane hydrolysis, namely, $HSiCl_3 \rightarrow HSi(OH)Cl_2 \rightarrow$ $\rightarrow HSi(OH)_2Cl \rightarrow HSi(OH)_3$ were studied[15] by the RHF/6-31G*, MP2/6-31G*, and MP4/6-31G* methods. The reaction mechanism assumes the formation of a pre-reaction complex $[H(OH)_xCl_ySi...OH_2]$ in each step (step *A*: $x = 0$, $y = 3$; step *B*: $x = 1$, $y = 2$; step *C*: $x = 2$, $y = 1$). In this complex, the coordination polyhedron of the silicon atom is a distorted trigonal bipyramid (TBP). The pre-reaction complex undergoes a transformation (*via* a TS containing a cyclic four-membered fragment [...H—O(H)—Si...Cl...] with a pentacoordinate Si atom) into a tetracoordinate silicon complex in which the HCl molecule forms a hydrogen bond with the OH group. This process corresponds to mechanism *c* and results in a product with retention of the "configuration" (substrate is optically inactive). The activation energies of the processes lie in the range from 33.9 to 40.8 kcal mol^{-1} depending on the hydrolysis step and computational method employed.[15] A study of the effect of an additional water molecule on the barrier to the reaction revealed an appreciable decrease in the barrier (to 4.5—25.5 kcal mol^{-1}), here, the second water molecule forms two hydrogen bonds, with a Cl atom and the first water molecule, being not coordinated to the silicon atom.[15] A decrease in the activation barrier to the hydrolysis of silanes upon an increase in the number of water molecules involved in the reaction from one to four was established in the RHF/6-31G* and B3LYP/6-31G* calculations of the reaction $MeSi(OMe)(OH)_2 \rightarrow MeSi(OH)_3$.[16] The silicon atom in the TS is pentacoordinate and its coordination number (CN) in the pre-reaction complex depends on the number of water molecules. Namely, CN = 4 in the presence of one or two H_2O molecules and CN = 5 in the presence of three or four H_2O molecules. The hydrolysis of $MeSi(OMe)(OH)_2$ corresponds to mechanism *c* and results in a product with retention of the "configuration" at the silicon atom.[16] The hydrolysis reactions of SiF_4 and $(HO)SiF_3$ with MP2 calculated activation barriers of 21 and 23 kcal mol^{-1}, respectively, proceed analogously.[17] The reactions begin with the formation of a pre-reaction complex containing a pentacoordinate Si atom and pass through cyclic four-membered TSs.[17] Possible pathways of the hydrolysis of $SiF_4(H_2O)_2$ intermediates with hexacoordinate silicon atoms were not explored in that study. Thus, according to the studies mentioned above, the hydrolysis of silanes involves the formation of a four-membered TS containing a pentacoordinate silicon atom and results in the products characterized by retention of the spatial arrangement of substituents at the silicon atom.

B3LYP and MP2 calculations of H_3SiF hydrolysis (reaction with one water molecule) revealed TSs with pentacoordinate silicon atoms corresponding to the processes with both retention (~30 kcal mol^{-1}) and inversion of the "configuration" (~80 kcal mol^{-1}). The last-mentioned process is specific to hydrolysis of hydrosilanes because the HF molecule that is formed in this case contains a hydrogen atom from the H_3SiF molecule.

At present, B3LYP and MP2 calculations[19] of the hydrolysis of H_3SiHal (Hal = F, Cl) provide an example of the most comprehensive theoretical study of hydrolysis of halosilanes. The authors of this study established the possibility of a process involving the formation of a hexacoordinate species. This reaction channel is characterized by the formation of an intermediate containing a pentacoordinate Si atom $H_2O...H_3Si—F...HOH$ (Hal = F) and a TS containing a hexacoordinate silicon atom $H_2O...H_3Si(...F)—O(H)—H^*$ (H^* forms a weak contact with the F atom). The activation energy of the reaction (Hal = F) lies between 30 and 35 kcal mol^{-1}, which is similar to the value found for the reaction involving one water molecule.[19] In the case of H_3SiCl hydrolysis the Si atom in the intermediate, $H_2O...H_3(Cl)Si...OH_2$, is hexacoordinate and the TS is similar to that found for H_3SiF hydrolysis. The reaction proceeds with retention of the "configuration". A hexacoordinate TS was also located, leading to the starting complex with inverted "configuration" at the silicon atom rather than to hydrolysis products.[19]

Thus, we believe that elucidation of all possible pathways of the hydrolysis reaction of the silanes containing more than one electron-acceptor group at the silicon atom requires a detailed study of the system SiF_4—H_2O, because tetrafluorosilane probably forms the most stable adducts with one and two water molecules.

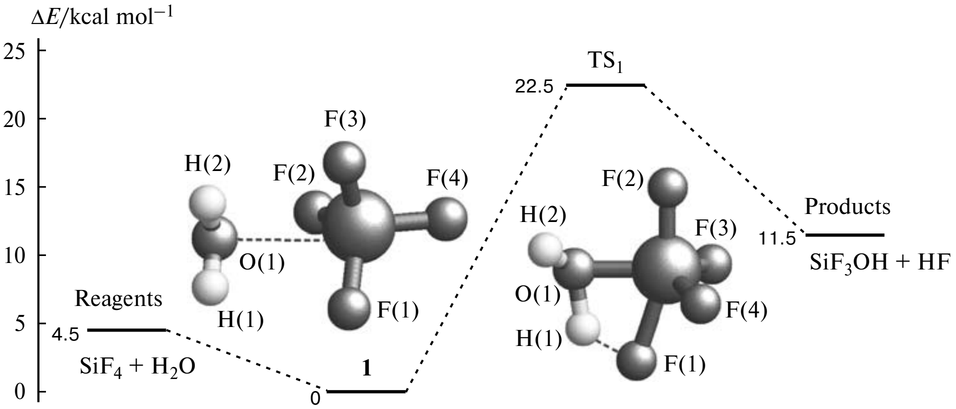

Fig. 1. Pathway *A* of SiF_4 hydrolysis; here and in Figs 2 and 3 the abbreviation "TS" stands for "transition state".

Table 1. Selected bond lengths (*d*) in reagents, intermediate **1**, transition structure TS_1, and products of SiF_4 hydrolysis following pathway *A*

Compound	*d*/Å							
	Si—F(1)	Si—F(2)	Si—F(3)	Si—F(4)	F(1)—H(1)	Si—O	O—H(1)	O—H(2)
SiF_4—H_2O	1.591	1.591	1.591	1.591	—	—	0.970	0.970
1	1.600	1.600	1.590	1.603	2.588	2.701	0.972	0.972
TS_1	1.934	1.631	1.599	1.606	1.215	1.789	1.174	0.973
SiF_3OH—HF	—	1.594	1.602	1.602	0.933	1.632	—	0.969

As mentioned above, only one pathway of the reaction of SiF_4 hydrolysis involving formation of a pentacoordinate TS was found earlier.[17] Hereafter, this reaction channel will be called pathway *A* (Fig. 1). In order to perform calculations in the famework of a unified computational approach, we optimized the geometries of intermediate **1** and transition state TS_1 (Table 1).

The energy characteristics of these species are shown in Fig. 1. Although the decomposition of compound **1** *via* TS_1 can lead to formation of complexes of the products of the type F_3Si—(H)O...H—F, their structure is insignificant from the standpoint of studying the first step of hydrolysis. As mentioned above, the reaction begins with a barrierless formation of a stable intermediate **1**, which can be treated as a loosely bound complex of water molecule with tetrafluorosilane. The coordination polyhedron of the silicon atom in compound **1** is a strongly distorted TBP with the water molecule in axial position. The Si—F_{eq} and Si—F_{ax} (F(4)) bond lengths differ only slightly. In the transition structure TS_1, the water molecule occupies an equatorial position, the Si—F(1) bond to be cleaved is appreciably lengthened, the leaving atom F being in an axial position of the TBP. Then, elimination of the HF molecule occurs. Hydrolysis of tetrafluorosilane is an endothermic process (see Fig. 1) with an activation energy of 22.5 kcal mol^{-1}, which is comparable with the published data (21 kcal mol^{-1}).[17]

It should be noted that no TS similar to TS_1 was located in the earlier theoretical studies[8—14] of the reactions of nucleophilic substitution using anionic species as nucleophiles. Probably, in this case a crucial role is played by hydrogen bonds and by the possibility of elimination of stable hydrogen fluoride molecule. The latter was confirmed in a recent study of the reaction of gas-phase decomposition of $PhSiF_3OH^-$, which results in the loss of either an HF or benzene molecule, but not the fluoride anion.[26]

We also found two additional channels of the reaction of SiF_4 hydrolysis with two water molecules (pathways *B* and *C*; Figs 2 and 3, respectively). They involve the formation of intermediates containing a hexacoordinate Si atom. The geometric parameters of the species are listed in Table 2. Complex **1** (see Fig. 1) that formed in the first step of pathway *B* adds the second water molecule, which leads to an intermediate **2** containing a hexacoordinate Si atom. The coordination polyhedron of the silicon atom in structure **2** has a shape of a distorted octahedron with *trans*-arrangement of two water molecules. Then, the HF molecule is eliminated from **2** *via* TS_3.

Pathway *C* differs from pathway *B* in structure of the key intermediate **5**, in which the coordination polyhedron of the Si atom is an octahedron with two *cis*-arranged water molecules. The reaction begins with a barrierless

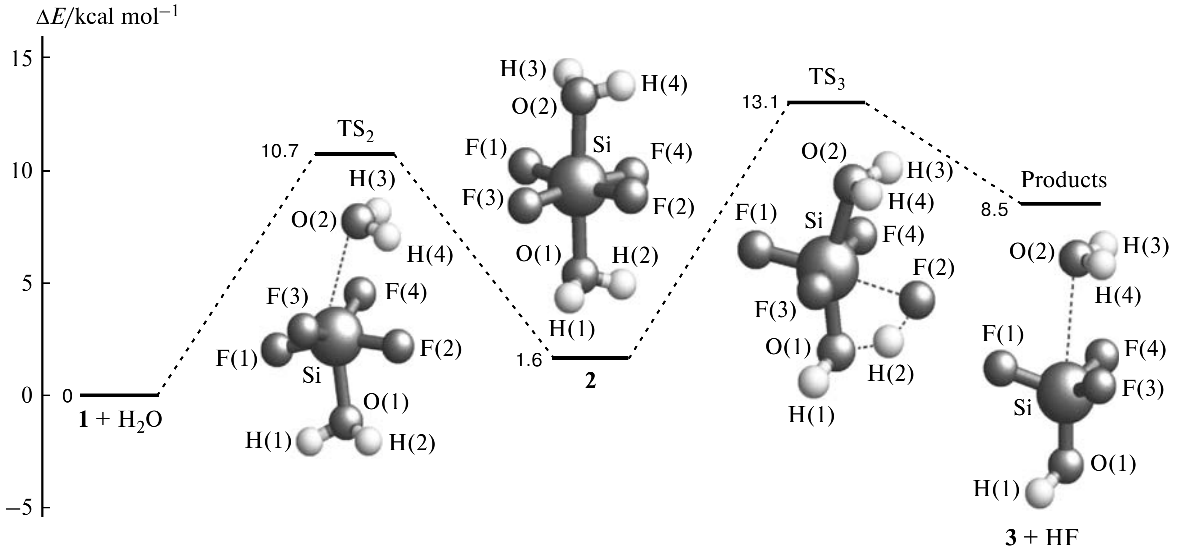

Fig. 2. Pathway *B* of SiF_4 hydrolysis.

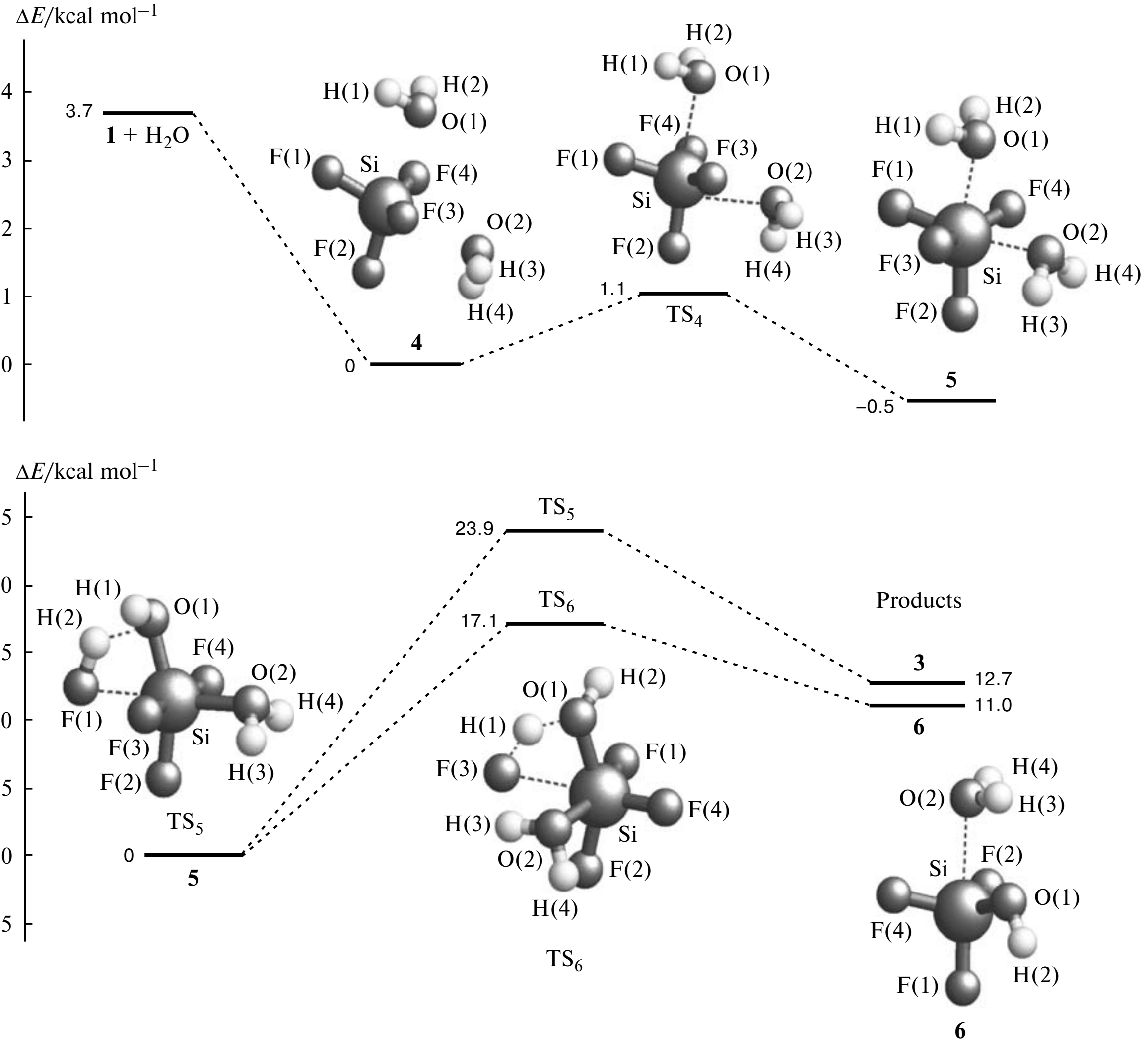

Fig. 3. Pathway *C* of SiF_4 hydrolysis.

Table 2. Selected bond lengths (*d*) in intermediates and transition structures of SiF_4 hydrolysis following pathways *B* and *C*

Bond	d/Å									
	2	**3**	**4**	**5**	**6**	TS_2	TS_3	TS_4	TS_5	TS_6
Si—F(1)	1.665	1.599	1.607	1.639	1.628	1.664	1.623	1.623	2.218	1.635
Si—F(2)	1.684	—	1.607	1.639	1.614	1.670	2.084	1.623	1.640	1.637
Si—F(3)	1.664	1.607	1.595	1.659	—	1.622	1.665	1.618	1.680	2.191
Si—F(4)	1.685	1.599	1.595	1.659	1.601	1.628	1.647	1.618	1.660	1.622
Si—O(1)	1.967	1.639	2.850	2.118	1.657	1.966	1.798	2.457	1.744	1.819
Si—O(2)	1.967	2.996	2.850	2.119	2.410	2.840	1.979	2.457	1.951	2.046
F(1)—H(2)	3.341	—	3.272	2.649	2.466	3.226	3.433	3.010	0.994	2.322
F(2)—H(2)	2.666	—	4.710	4.135	3.374	2.280	1.159	4.363	3.179	3.883
F(3)—H(1)	2.333	3.044	3.356	2.376	—	3.132	2.450	2.882	2.202	1.160
O(1)—H(1)	0.978	0.969	0.972	0.976	—	0.976	0.975	0.974	0.973	1.226
O(1)—H(2)	0.978	—	0.972	0.976	0.971	0.976	1.247	0.974	1.581	0.976

formation of intermediate **4**, which undergoes transformation into intermediate **5** *via* TS_4. The structures TS_4, **4**, and **5** differ in lengths of the Si—O(1) and Si—O(2) contacts, which decrease in the order **4** < TS_4 < **5** (see Table 2). The coordination polyhedron of the silicon atom also changes its shape from a tetrahedron to octahedron. Following pathway *C*, two isomeric TSs of the decomposition of intermediate **5** are possible, namely, TS_5 and TS_6. In the former the leaving group (F) and the loosely bound ligand (additional water molecule) are *trans*-arranged relative to each other, while in the latter they are *cis*-arranged, which is 6.25 kcal mol^{-1} more preferable. If we exclude the atoms of the leaving molecule (HF) from the transition structures TS_3, TS_5, and TS_6, the geometries of the remaining parts will correspond to that of the TS of pseudorotation according to Berry reported for the anions containing a pentacoordinate silicon atom.[27,28] It is important that the pathways of SiF_4 hydrolysis in the presence of one and two water molecules studied in this work lead to SiF_3OH with formal retention of the "configuration" at the silicon atom. With allowance for the published data[19] we can conclude that hydrolysis of silanes always occurs with retention of the «configuration» of substituents at the silicon atom. It is likely that inversion of the "configuration" at the silicon atom can be realized under the action of anions or strong neutral bases that react with silane to give stable complexes capable of experiencing pseudorotation according to Berry.

Thus, hydrolysis of SiF_4 is an endothermic process. The lowest activation barrier was found for the pathway *B*, which involves formation of an intermediate with *trans*-arranged water molecules. Complexes **1**, **2**, **4**, and **5** containing penta- and hexacoordinate Si atoms seem to be the most probable intermediates. Further transformations of these species are only possible in the presence of additional water molecules or a reagent that can efficiently bind the HF formed.

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