Hydrogenation of the silanone groups (≡Si—O)$_2$Si=O. Experimental and quantum-chemical studies

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The reactivity of bis(siloxy)silanone groups (≡Si—O)$_2$Si=O stabilized on a silica surface with respect to H_2 molecules was studied. The reaction was found to give the (≡Si—O)$_2$SiH(OH) groups. The rate constant for this process was determined. Its activation energy in the 300—580 K temperature range is 13.4±0.3 kcal mol^{-1}, and the enthalpy is 54±5 kcal mol^{-1}. The activation energy for the reverse reaction, *viz.*, elimination of a hydrogen molecule, is equal to ~65 kcal mol^{-1}. Quantum-chemical calculations of hydrogenation of $F_2Si=O$ and $(HO)_2Si=O$, which are the simplest molecular models of the silanone groups, were performed. Data on the geometrical and electronic structures of transition states and on the effects of substituents at the silicon atom on the reactivity of the silanone groups in this process were obtained. The optical absorption band of the surface silanone groups was quantitatively characterized. Its maximum is located at 5.65±0.1 eV; the extinction coefficient at the maximum ε(220 nm) is (3±0.5) · 10^{-18} cm^2 molec.$^{-1}$.

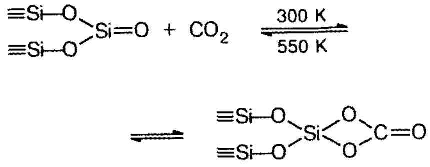
Key words: silanone, hydrogenation, quantum-chemical calculations.

Information on the structures, spectral characteristics, and reactivities of highly reactive intermediates, *viz.*, free radicals, compounds incorporating low-coordinated atoms, *etc.*, is needed in various branches of physical chemistry. However, experimental studies on this line are usually associated with solution of complex methodical problems. They are mostly due to the difficulty of stabilization and detection of these species. The above refers completely to the silanones $X_2Si=O$.

Compounds containing an >Si=O group were identified for the first time by IR spectroscopy using the low-temperature matrix isolation technique.[1—5] Unlike carbonyl groups, the silanone groups (SG) >Si=O were found to undergo oligomerization even at very low temperatures, *i.e.*, they are highly reactive. Since these groups are difficult to obtain and stabilize, experimental data on the mechanisms of reactions involving SG and, especially, quantitative characteristics of these reactions (rate constants and activation energies) are scarce. This stimulated the quantum-chemical calculations dealing with the properties and reactivities of molecules incorporating SG, mainly $H_2Si=O$.[6—12] However, the calculations cannot fill the gap caused by the absence of experimental results.

The low-temperature matrix isolation technique, which was used to obtain the main data on silanones, is based on the stabilization of reactive species in an inert matrix. A method has been proposed[13—15] for the preparation of reactive intermediates stabilized on (grafted to) the surface of a solid (SiO_2). It was shown that this method allows one to prepare various types of reactive intermediates[16] including SG-containing structures (≡Si—O)$_2$Si=O. Initially, they were detected[17] on a mechanically activated SiO_2, and later, a method for preparing them on thermochemically activated silica [so-called "reactive silica" (RSi)[18]] was developed. In the latter case, these structures were obtained[18] by oxidation of the silylene groups (≡Si—O)$_2$Si:.

Silanone groups stabilized on the surface of a solid are stable up to 700 K and are accessible to molecules from the gas phase. This is very convenient for investigating their reactivity. They were found[17,18] to react with CO_2 molecules giving the corresponding monodentate carbonates [reaction (1)].



(1)

A similar reversible complex formation also occurs[17] between SG and N_2O molecules. Oxidation of SG (2) in an atmosphere of nitrogen(I) oxide proceeds at a lower rate.[19]

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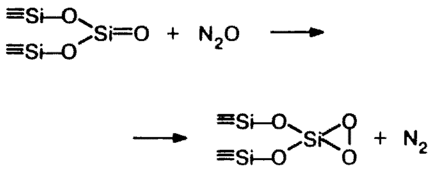


(2)

SG proved to be efficient acceptors of low-molecular-weight free radicals. The structures of the products of the addition of $H^{\cdot}(D^{\cdot})$, $^{\cdot}CH_3$, $^{\cdot}C_2H_5$, and *cyclo*-$^{\cdot}C_3H_5$ radicals to SG have been identified.[14,17,19,20] These reactions occur at high rates even at 77 K and, hence, their activation energies are relatively low.

In this work we continued studies on the reactivity of SG. We present the results of our study dealing with the mechanism and kinetic features of the interaction of SG $(\equiv Si{-}O)_2Si{=}O$ with H_2 molecules. To the best of our knowledge, experimental data concerning this process are absent in the literature. Only the results of quantum-chemical calculations of the reaction involving the simplest silanone $H_2Si{=}O$ have been reported.[10—12]

It can be suggested that the $(\equiv Si{-}O)_2Si{=}O$ group in which a silicon atom is bound to two electronegative substituents ($\equiv$Si—O) differs in its physicochemical properties from the $H_2Si{=}O$ molecule. It was shown[21] that the physicochemical characteristics of fluoro-substituted low-molecular-weight silicon compounds are similar to those of the corresponding groups on a silica surface. Therefore, we carried out quantum-chemical calculations for the hydrogenation of $F_2Si{=}O$ and $(HO)_2Si{=}O$ molecules. This made it possible to obtain information on the geometric and electronic characteristics of the reactants, transition states, and reaction products and to analyze the effect of the substituents on the reactivity of SG in this reaction.

Experimental

The procedure used for the preparation of RSi was close to that described previously.[22,23] Aerosil A-300 with an initial specific surface area of ~300 $m^2\ g^{-1}$ was used as a powder or as pressed semitransparent ~50 mm thick pellets.[24] The use of "film" samples made it possible to control the processes involving SG by optical methods (for more details, see below).

A weighed sample of Aerosil was placed in a quartz vessel connected to a high-vacuum system, and calcined in an atmosphere of oxygen at 1200 K (in order to remove chemisorbed compounds from the oxide surface). Then the silica surface was methoxylated at 675—725 K in a methanol vapor (~10^4 Pa) for 15 min, and the sample was subjected to vacuum pyrolysis. The sample was heated to the final temperature (1200—1250 K) over a period of ~60 min and kept at this temperature for ~20 min. This afforded a silica (RSi) sample possessing enhanced chemisorption activity.[23]

The gas pressure in the system was controlled by a Pirani gage, when it was below 0.1 Pa, and by a membrane manometer, when it was above this value. The optical absorption spectra of the "film" samples were recorded on a Specord M-40 spectrophotometer (in the 1.5—6.5 eV region). The IR spectra of the products of hydrogenation of SG were also recorded using "film" samples of activated Aerosil. The gases used in the experiments (H_2, D_2) were purified by passing them through activated porous sorbents cooled to 77 K. The reactants were no less than 99 % pure.

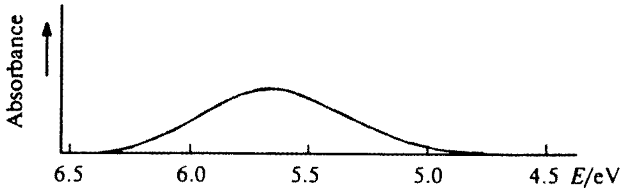
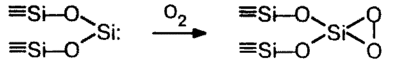


Fig. 1. Optical absorption spectrum of $(\equiv Si{-}O)_2Si{=}O$ groups.

Quantum-chemical calculations were carried out by the *ab initio* SCF MO LCAO method using the GAUSSIAN program.[25] The molecular geometry was optimized by minimizing the gradient norm using the split valence 6-31G** basis set. Transition states were characterized by one negative eigenvalue of the Hessian matrix. The energies of the optimized structures were refined in terms of the second-order Meller—Plesset perturbation theory (MP2/6-31**//RHF/6-31*$^{(*)}$) (at this level of calculations, the electronic correlation was taken into account only for valence electrons). The vibrational spectra of the structures and of transition states studied were calculated in a harmonic approximation using the 6-31G* or 6-31G** basis set.

Results and Discussion

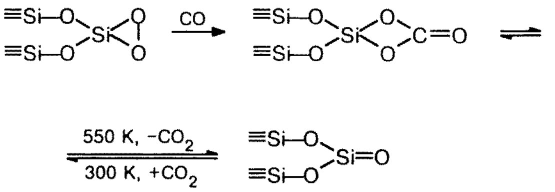
Preparation and optical characteristics of the $(\equiv Si{-}O)_2Si{=}O$ groups. The surface of RSi samples mostly contains stabilized silylene groups $(\equiv Si{-}O)_2Si{:}$.[18,26] The concentration of these groups is ~10^{13} cm^{-2}. These groups are responsible for an intense optical absorption band with a maximum at ~5.3 eV.[16,18] In an atmosphere of O_2, silylenes are converted into dioxasiliranes [reaction (3)].[18,26]



(3)

The optical absorption spectrum of the latter[18,19] consists of two broad low-intensity bands with maxima at ~5 and ~3 eV. The amplitudes of the corresponding lines are more than an order of magnitude lower than those for silylene groups.

The silanones were obtained from dioxasiliranes by a previously described procedure[18,26] (reaction (4)).



(4)

In the first stage, a monodentate carbonate structure is formed as a result of the chemisorption of CO. No noticeable optical absorption of this group was detected in the 1.5—6 eV range.

At temperatures above 550 K, the carbonates decompose with the elimination of CO_2 and formation of silanones.[17,18] The $>Si=O$ group accounts for the optical absorption band with a gently sloping maximum near 5.65±0.1 eV and a half-height width of ~0.9 eV (Fig. 1). The intensity of this band increases in parallel with the amount of the thermodesorbed CO_2 molecules. The maximum of the optical absorption band corresponding to the silanone sites is located at higher energies than was reported previously.[17*]

The extinction coefficient of the silanone sites at the optical absorption maximum was $\varepsilon(220 \text{ nm}) = (3\pm0.5) \cdot 10^{-18}$ cm^2 molec.$^{-1}$ This was determined from the correlation of the optical density of the absorption band and the number of CO_2 molecules chemisorbed by the sample or thermodesorbed from it [see reaction (4)].

The optical transition oscillator strength is related to the integral absorption coefficient $K = \int\varepsilon(\nu)d\nu$ by the relationship[27]

$$f = 2.59 \cdot 10^{12} \cdot F \cdot \int\varepsilon(\nu)d\nu,$$

where F is a multiplier taking into account the effect of the medium in which the site is located (normally $F = 1$ is taken). The oscillator strength of the corresponding optical transition estimated from the above equation ($F = 1$) amounts to 0.045±0.01.

Kinetic regularities of the reaction ($(\equiv Si-O)_2Si=O + H_2$ (D_2)). When a sample is kept in an atmosphere of H_2 (D_2), the intensity of the optical absorption of SG decreases. The corresponding kinetic curve is shown in Fig. 2 (D is the optical density at 220 nm) in the coordinates of a second-order equation [$D \sim N(>Si=O)$]:

$$-dN(>Si=O)/dt = K \cdot p(H_2) \cdot N(>Si=O).$$

This law holds satisfactorily up to a degree of conversion of more than 80 %. The rate constant for the reaction at this temperature is $(3.2\pm0.2) \cdot 10^{-22}$ cm^3 molec.$^{-1}$ s^{-1}.

In the temperature region above room temperature, the rate of hydrogenation of SG was monitored by the chemisorption method. The overall number of hydrogen molecules chemisorbed in this process was found to be close to the number of SG in the sample. This was also determined independently from the amount of chemisorbed CO_2 [see reaction (4)). Thus, one hydrogen (deuterium) molecule reacts with one SG.

The kinetic curves for the absorption of hydrogen by the sample are satisfactorily linearized in the (N_0/N—$\ln\Phi$) coordinates, where $\Phi = \int p(H_2)dt$ is proportional to the number of collisions of gas molecules over time t with a surface site. This means that the kinetics of hydrogenation follows a bimolecular law. From the slopes of these straight lines, the rate constants for the hydrogenation of the SG were determined in the 395—580 K temperature range.

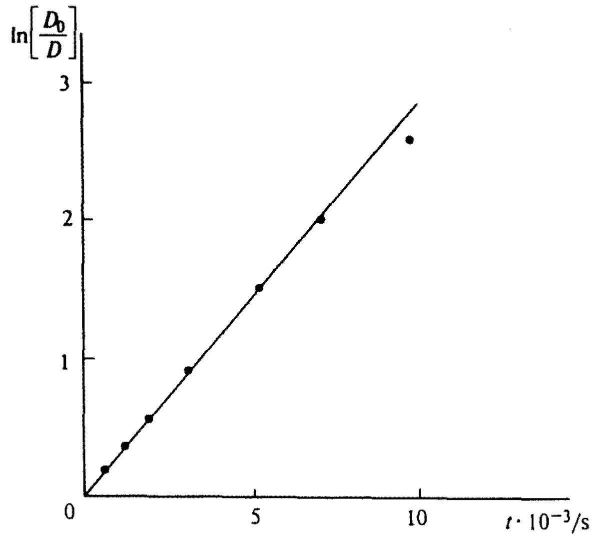


Fig. 2. Variation of the intensity of the optical absorption band of SG during hydrogenation [$p(H_2)$ = 28 Torr, T = 296 K].

Figure 3 presents the temperature dependence of the rate constant of hydrogenation (K) in the 300—580 K temperature range. In the Arrhenius form, this dependence is written as follows:

$$K = (2.5\pm0.2) \cdot 10^{-12} \cdot \exp(-(13.4\pm0.3) \text{ (kcal mol}^{-1})/RT) \text{ (cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}).$$

Note that the preexponential factor in this expression has a reasonable value. Thus, the activation energy for the hydrogenation of the $(\equiv Si-O)_2Si=O$ groups is ~13 kcal mol^{-1}.

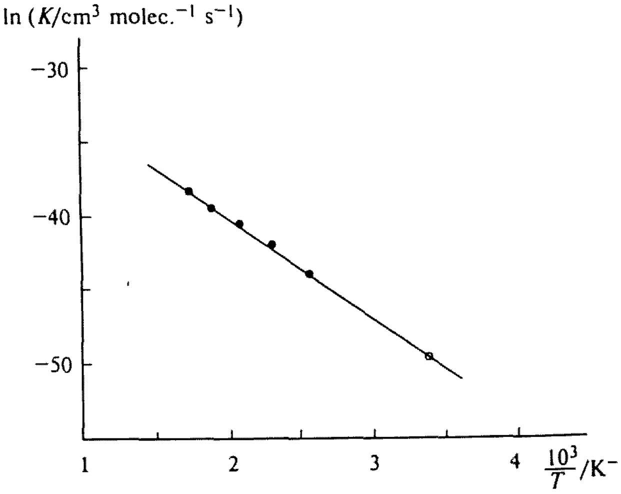


Fig. 3. Temperature dependence of the rate constant for the hydrogenation of SG (full circles show the values obtained by chemisorption measurements, and the white circle corresponds to optical measurements).

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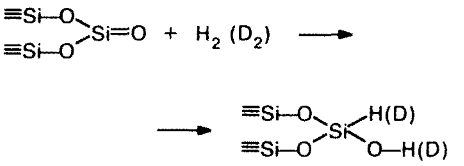
* Powdered samples of mechanically activated silica were used;[17] the optical absorption spectra of SG were recorded in diffuse light without allowance for its scattering by the sample, which could lead to distortions of spectral patterns.

An IR spectroscopic study has shown[23,28] that two new absorption bands with maxima at 3741 and 2270 cm^{-1} appear during this reaction. Evidence was presented[28] that these bands correspond to the $(\equiv Si-O)_2Si(H)OH$ group, and their appearance is due to the formation of the products of hydrogenation of SG [reaction (5)].

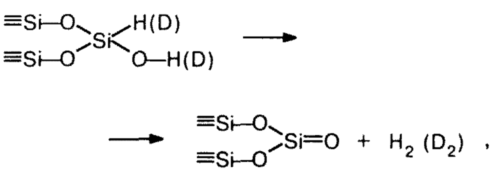

(5)

Previously these absorption bands recorded for the surface of activated silica were interpreted[23] in terms of another structure of the chemisorption site; therefore, they were assigned to groups of a different chemical nature (for more details, see Refs. 18 and 26).

The integral intensities of the absorption bands corresponding to the newly formed hydroxyl and silane groups are commensurable (they differ by less than 50 %).[29] Since the band widths also do not differ too much, this means that the extinction coefficients for the corresponding groups are also similar. In one of the experiments, the SG were obtained [see reaction (3)] using oxygen enriched in the ^{18}O isotope. The spectrum recorded after hydrogenation of this sample exhibits a band at 3725 cm^{-1}, which should be assigned to the stretching vibrations of the $^{18}O-^{1}H$ bond in the $\equiv Si-OH$ group.

Heating of hydrogenated samples at temperatures above 850 K leads to the appearance of low-molecular-weight products in the gas phase. It was shown by mass spectrometry that thermodesorption affords molecular hydrogen as the major product. The results of volumetric measurements indicate that the number of desorbed molecules corresponds to the number of gas molecules chemisorbed by the sample during hydrogenation with an accuracy of no less than 15 %.

After thermodesorption, $>Si=O$ groups were detected on the oxide surface. Their concentration was determined by the volumetric method from the amount of carbon dioxide chemisorbed by the sample [see reaction (4)]. The number of regenerated groups proved to be several times lower than their initial number. This decrease is due to the destruction of SG at high temperatures.[17,18,26] Thus, at elevated temperatures, dehydrogenation (6), the reverse process with respect to hydrogenation (5), occurs,


(6)

which is complicated by the destruction of the SG formed.

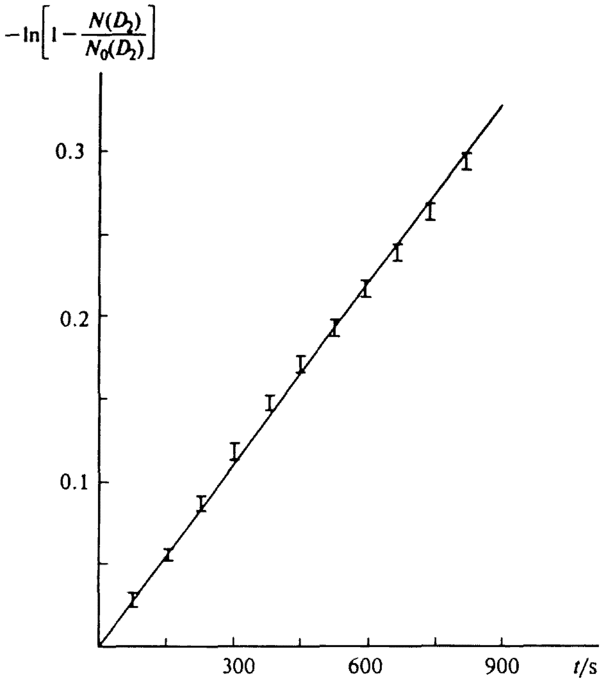


Fig. 4. Kinetic curve for the evolution of D_2 during thermal decomposition of $(\equiv Si-O)_2Si(D)OD$ groups [T = (873±10) K].

Figure 4 presents the initial section of the kinetic curve for the evolution of D_2 [$N(D_2)$] at T = (873±10) K during the thermal decomposition of the $(\equiv Si-O)_2Si(D)OD$ groups [the initial number of these groups is $N_0(D_2)$] [see reaction (6)]. This plot is described satisfactorily by a first-order equation with the rate constant equal to $(3.6\pm0.5)\cdot10^{-4}$ s^{-1}. Assuming that the preexponential factor for this unimolecular process is 10^{13} s^{-1} [$K = 10^{13}\cdot\exp(-E_a/RT)$ s^{-1}], its activation energy can be estimated as E_a = 66±2 kcal mol^{-1}. From the activation energies for reactions (5) and (6), we can find the enthalpy of hydrogenation of SG, which is equal to 52.5±3 kcal mol^{-1}.

Table 1 presents the results of calorimetric studies of the enthalpy of the hydrogenation of SG in which powdered samples of activated Aerosil were used. The measurements were carried out at 463 K. Simulta-

Table 1. Results of calorimetric measurements of the heats of hydrogenation of $(\equiv Si-O)_2Si=O$ groups

Number of hydrogen molecules chemisorbed by the sample, $N\cdot10^{-17}$	Enthalpy of the reaction/kcal mol^{-1}
2.5	54.8
2.55	59.9
2.9	63.5
3.1	43.0
2.7	53.6
	$\Delta\bar{H}$ = 54.5±5

neously, the amount of chemisorbed gas was recorded (based on the pressure variation in the system) and the amount of heat evolved was measured (microcalorimetric measurements).[30] One portion of the chemisorbed gas corresponded to a small part of the total number of SG in the sample. The average value obtained for the enthalpy was ~55 kcal mol^{-1}. This is in good agreement with the value of the enthalpy of this process found from our kinetic results (see above).

Results of quantum-chemical calculations of the process $X_2Si=O + H_2 \rightarrow$ Transition state (TS) $\rightarrow$ $X_2Si(H)OH$ (X = H, OH, F). The physicochemical parameters, *viz.*, spectral, thermochemical, and kinetic characteristics, of silica surface groups [($\equiv$Si—O)$_2$SiXY, ($\equiv$Si—O)$_3$SiX] are remarkably close to those of the corresponding low-molecular-weight compounds in which the ($\equiv$Si—O) fragments have been replaced by fluorine atoms (F_2SiXY, F_3SiX).[21] Hence, experimental data obtained for processes involving sites of one type can be used for the approximate characterization of the reactivities of other types of sites. When no relevant data have been reported in the literature, which is, as a rule, the case with silicon-containing compounds, data on their reactivities can be obtained by quantum-chemical methods, which are now fairly accurate. In this section, we present the results of quantum-chemical calculations carried out for the hydrogenation of fluorine-, hydroxyl-, and hydrogen-containing silanones. Previously,[8] similar calculations were carried out for $H_2Si=O$; the results of these calculations are included in Tables 2—5 for comparison.

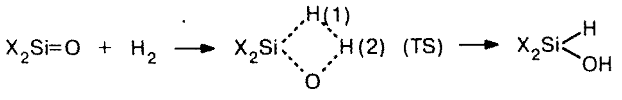
The adiabatic potential energy surface of the $(HO)_2Si=O$ molecule (RHF/6-31G* calculations) contains three local minima corresponding to different orientations of the silanol group (see also Ref. 9).* This is confirmed by calculation of the vibrational spectra of the conformers. The molecule is planar in all three states (see Table 2). Two of these states have the C_{2v} symme-

Table 2. Geometrical characteristics of $X_2Si=O(1)$ molecules

X	Bond length/Å			Angle/deg			
	Si—O(1)	Si—X	O—H	O(1)SiX	XSiX	SiOH	O(1)SiOH
H (C_{2v})	1.498	1.469	—	124.5	111.1	—	—
OH (**A**) (C_{2v})	1.493	1.604	0.949	127.4	105.2	116.8	0.0
OH (**B**) (C_s)	1.490	1.613, 1.602	0.949, 0.948	126.3, 127.7	106.0	117.1, 118.7	0.0, 180.0
OH (**C**) (C_{2v})	1.489	1.611	0.946	124.9	110.3	—	180.0
F* (C_{2v})	1.482 (1.524)	1.556 (1.587)	—	127.6 (127.7)	104.8 (104.6)	—	—

* The results of calculations in the MP2/6-31G** approximation are given in parentheses.

Table 3. Geometrical characteristics of the transition states (TS) of the reaction*



X	Bond length/Å					Angle/deg					
	SiO	SiH(1)	OH(2)	H(1)H(2)	SiX	H(1)SiO	H(2)OSi	H(1)H(2)O	H(2)H(1)Si	XSiX	δ**
H (C_s)	1.549	1.766	1.438	0.960	1.476	85.4	67.5	139.2	67.9	109.3	16.7
OH (**A**) (C_s)	1.544	1.732	1.409	0.945	1.605	84.0	68.7	137.0	70.3	106.7	19.1
OH (**B**) (C_1)	1.538	1.735	1.418	0.936	1.612, 1.602	84.5	68.0	137.1	69.0	107.5	18.7
OH (**C**) (C_s)	1.533	1.736	1.429	0.932	1.609	84.9	67.8	138.0	69.3	111.8	18.7
F (C_s)	1.527	1.721	1.459	0.958	1.559	87.4	67.1	136.0	69.5	106.1	19.4

* Parameters of the hydroxyl groups: R(O—H) = 0.948 (**A**) (0.941 (**C**)) Å, ∠HOSi = 117.8° (**A**) (124.8° (**C**)), ∠HOSiO = 168.9° (**A**) (−10.4° (**C**)), their hydrogen atoms and the oxygen atom of the SG in the TS deviating from the (—O)$_2$Si plane in one direction for conformer **A** and in different directions for conformer **C** (see Fig. 5).

** δ is the angle showing the deviation of the oxygen atom in the TS from the XSiX plane.

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* Three minima were also localized at the potential energy surface of $(HO)_2Si$ as found by RHF/6-31G* calculations. The minima correspond to planar conformers, two of which have the C_{2v} symmetry (*trans,trans-* (**A'**) and *cis,cis-* (**C'**) orientation of H, O, Si, O, and H atoms) and the third has the C_s symmetry (*cis,trans-* (**B'**) configuration) (see also Ref. 11). Conformer **B'** possesses the lowest energy. The relative ΔH(0) values for structures **A'**, **B'**, and **C'** are 0.0, −2.6, and −0.1 kcal mol^{-1}, respectively (the MP2/6-31G* method).

Table 4. Geometrical characteristics of the hydrogenation products $X_2Si{<}^{H(1)}_{O(1)H}$

X	Bond length/Å					Angle/deg				
	SiH(1)	SiO(1)	O(1)H	SiX	OH	H(1)SiO(1)	H(1)SiX	SiOH	H(1)SiO(1)H	H(1)SiOH
H (C_s)	1.475	1.641	0.946	1.484	—	106.8	111.6	—	180.0	—
O(H) (C_1)	1.462	1.632	0.947	1.633, 1.641	0.947, 0.947	105.6	113.2, 110.8	117.0, 119.0	158.1	105.7, 60.5
F* (C_s)	1.450 (1.462)	1.614 (1.638)	0.947 (0.970)	1.579 (1.604)	—	109.3 (107.9)	110.5 (110.6)	—	180.0 (180.0)	—

* The results of calculations in the MP2/6-31G** approximation are given in parentheses.

try and are characterized by the *cis-* (structure **A**) or *trans-* (structure **C**) orientation of the hydroxyl groups with respect to the Si=O fragment. The third structure has the C_s symmetry with different (*cis-* and *trans-*) orientations of the OH groups (structure **B**).

Form **A**, in which the H atoms of the hydroxyl groups are the most remote from each other, possesses the lowest energy, and conformer **C** possesses the highest energy. According to the results of calculations (MP2/6-31G*), the relative $\Delta H(0)$ values for structures **A**, **B**, and **C** are 0.0, 1.4, and 7.5 kcal mol^{-1}, respectively.

The MO corresponding to the silicon—oxygen π-bond in SG, is largely composed of the $2p_z$-AO of the oxygen atom, whereas the contribution of the $3p_z$-AO of the silicon atom is small (the Z axis is perpendicular to the symmetry plane of the molecule). This accounts for the facts that the π-bond in the >Si=O group is substantially weaker than that in the >C=O group and that the former is more reactive.[6—8]

According to the results of quantum-chemical calculations, the highest occupied MO (HOMO) in $H_2Si=O$ is populated by the unshared electron pair of the oxygen atom, whereas this orbital in $(HO)_2Si=O$ or $F_2Si=O$ is occupied by the electron pair of the silicon—oxygen π-bond. However, the difference between the energies of these MO is small. This differs sharply from the situation observed for >C=O group in which the unshared electron pair of the oxygen atom occupies an MO whose energy is markedly higher.

The optimized geometrical characteristics of the reactants, transition states, and reaction products are listed in Tables 2—4. Figure 5 shows the arrangement of atoms in the transition states corresponding to the hydrogenation of various conformers of the $(HO)_2Si=O$ molecule.

The hydrogen, silicon, and oxygen atoms in the transition states are located in the same plane forming an irregular quadrangle. This arrangement ensures the most favorable conditions for the overlap of the HOMO with the lowest unoccupied MO (LUMO) of an SG and a hydrogen molecule.* The hydrogen molecule is strongly polarized in the transition state (charges on the atoms are 0.3—0.4, the molecule as a whole being electrically

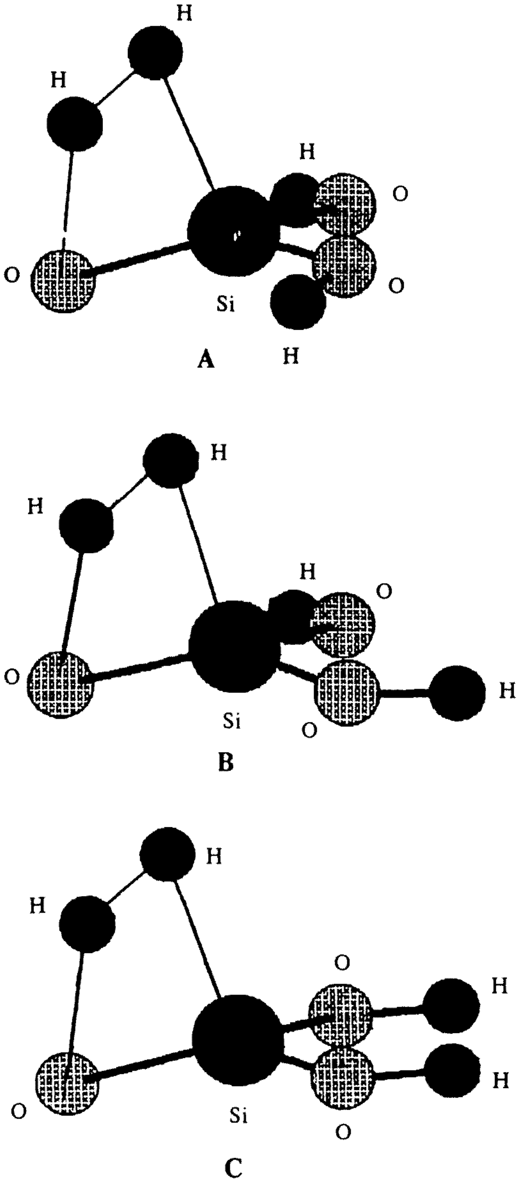

Fig. 5. Transition states for the hydrogenation of various conformers of the $(HO)_2Si=O$ molecule.

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* The $3p_z$-AO of the silicon atom makes the greatest contribution to the LUMO, corresponding to loosening of the π-bond of SG. The HOMO and the LUMO in the hydrogen molecule are the bonding and antibonding combination of the 1s-AO.

Table 5. Energy characteristics of the $X_2Si{=}O + H_2 \rightarrow TS \rightarrow X_2SiH(OH)$ process*

X	Parameter	$X_2Si{=}O$	TS	$X_2SiH(OH)$
H	$-E$	365.19536	366.31051	366.42153
	ZPE	12.3	19.0	22.4
	$\Delta E(0)$	0	26.7	−43.0
	$\Delta H_0(0)$	0	27.5 (29.8)	−38.8 (−38.4)
HO	$-E$	515.40284	516.52933	516.62984
(A)	ZPE	19.8	28.2	30.8
	$\Delta E(0)$	0	19.6	−43.5
	$\Delta H_0(0)$	0	22.1	−38.4
HO	$-E$	515.40079	516.52841	516.62984
(B)	ZPE	19.8	28.6	30.8
	$\Delta E(0)$	0	18.9	−44.8
	$\Delta H_0(0)$	0	21.8	−39.7
HO	$-E$	515.39072	516.52019	516.62984
(C)	ZPE	19.9	28.0	30.8
	$\Delta E(0)$	0	17.7	−51.1
	$\Delta H_0(0)$	0	20.3	−45.7
F	$-E$	563.37402 (563.37910)	564.51084 (564.51364)	564.62646 (564.62789)
	ZPE	5.6	13.9	17.4
	$\Delta E(0)$	0	13.1 (14.5)	−59.5 (−57.2)
	$\Delta H_0(0)$	0	15.5 (16.9)	−53.6 (−51.3)

* Total energies (E) calculated at the MP2/6-31G**//RHF/6-31G** level for TS and at MP2/6-31G**//RHF/6-31G* level for other structures are expressed in au, and the other values are expressed in kcal mol^{-1}; the energy of H_2 is −1.15766 au. The results[8] of an MP4/MC311G**//MP2/6-31G** calculation for X = H and of an MP2/6-31G** calculation for X = F are given in parentheses. The zero point vibration energies (ZPE) were calculated in a harmonic approximation using the 6-31G* or 6-31G** basis set and scaled with the coefficient 0.89 [10–12]. For H_2, ZPE = 5.9 kcal mol^{-1}.

neutral). The activation (elongation) of the H—H bond is accompanied by the synchronous formation of O—H and Si—H bonds.

Table 5 lists the energy characteristics of the processes. Note that the calculations carried out for $H_2Si{=}O$ at a higher theoretical level,[10] did not result in substantial variations of the energy characteristics of the reactions. This was also confirmed by calculations of hydrogenation of $F_2Si{=}O$ carried out by various procedures (see Table 5). The enthalpies of hydrogenation of different conformers of $(HO)_2Si{=}O$ were calculated on the assumption that the reaction product $(HO)_3Si{-}H$ exists in its most stable form (symmetry C_1) in all cases.

The appearance of electronegative substituents at the silicon atom in the series $H_2Si{=}O$, $(HO)_2Si{=}O$ (**A**, **C**) and $F_2Si{=}O$ results in a noticeable decrease in the activation energy and an increase in the enthalpy of hydrogenation. These variations correlate with the decrease in the strength of the Si=O bond over this series. According to MP2/6-31G* calculations, the enthalpies $[\Delta H(0)]$ of the reaction $X_2Si{=}O \rightarrow X_2Si(^1A_1) + O(^3P)$ in this series amount to 144.3, 130.0, 122.4, and 118.2 kcal mol^{-1}. It can be assumed that these values are ~10 kcal mol^{-1} lower than the actual strengths of the Si=O bonds in these molecules.*

Among the calculated activation energies and enthalpies of hydrogenation, those for the difluorosilanone are the closest to the experimental results presented in the preceding section. This is in agreement with the previous statement that the properties of groups stabilized on silica surface are similar to those of their low-moleclar-weight fluorine-substituted analogs.[21] The results of our quantum-chemical calculations confirm the conclusion[21] that even the use of the smallest low-molecular-weight silicon compounds containing electronegative substituents (F, HO) makes it possible to satisfactorily represent the properties of the surface defects of silica.

In the case of reactions occurring in viscous disordered media, including heterogeneous processes, groups with identical chemical structures can differ in reactivity. This results in the specific kinetic features of reactions observed in these systems.[31,32] In the case of the SG $(\equiv Si_\beta{-}O)_2Si{=}O$ stabilized on the surface of amorphous silica, these distinctions can largely be associated with the spatial arrangement of the β-silicon atoms. The positions of the latter are governed by the structure of the solid and can be dissimilar for individual sites stabilized on the amorphous silica surface, which should also affect the reactivity of these groups.

According to our experimental results (see above), the rate of hydrogenation of SG is properly described by a second-order equation (see Fig. 2). It thus follows that the differences in the activation energies for the addition of a hydrogen molecule to the surface sites are no more than 1 kcal mol^{-1}. This indicates either that their conformations are similar or that the spatial arrangement of the β-substituents has only a slight effect on the reactivity of SG.

At present, the spatial structure of the surface SG from the above standpoint is obscure. An idea of the relationship between the spatial structure of a site and its reactivity can be inferred from quantum-chemical calculations. In fact, variations of the positions of the β-substituents (hydrogen atoms) in the $(HO)_2Si{=}O$ molecule (*i.e.*, the orientation of its hydroxyl groups) have an effect on the activation energy of hydrogenation. However, this effect is relatively slight: the variation of the activation energy of hydrogenation on passing from conformer **A** to **C** does not exceed 2 kcal mol^{-1}. These data suggest that even substantial distinctions in the arrange-

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* The strength of the corresponding bond in $H_2Si{=}O$ determined by G-2 calculations[11] was 155.4 kcal mol^{-1}. Calculations by this method make it possible to estimate the heats of formation of molecules with a "chemical" accuracy of ±1 kcal mol^{-1}.

ment of the β-substituents would hardly affect substantially the reactivity of the surface SG.

Much greater distinctions in the spectral and other physicochemical properties have been found for the silylene sites $(\equiv Si-O)_2Si$: stabilized on the surface of RSi samples.[24] In the case of SG, these differences are largely levelled. A similar decrease in the distinction between the reactivities of groups grafted to a solid surface with an increase in the number of chemical bonds separating the active site and the surface atom of the solid has been noted previously.[33]

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