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Mechanisms of Heterogeneous Processes in the System $SiO_2 + CH_4$: II. Methylation of >Si=O Groups

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Abstract—The methods of optical and IR spectroscopy and quantum chemistry were used to obtain data on the direction and kinetics of the reaction of a silanone $(\equiv SiO)_2Si{=}O$ with a CH_4 molecule and a methyl radical. Two mechanisms of methylation of silanone groups, molecular and free-radical, are studied. Both processes are accompanied by the formation of $(\equiv SiO)_2Si(OH)(CH_3)$ groups. The rate constant of the molecular process is determined and its activation energy is estimated (17 kcal/mol). A methyl radical adds to the silicon atom in a silanone group to form the oxy radical $(\equiv Si–O)_2Si(O^{\bullet})(CH_3)$. This radical carries a free-radical process of silanone group methylation. The main channel for the pyrolysis of $(\equiv Si–O)_2Si(OH)(CH_3)$ groups is their decomposition with the abstraction of a methane molecule. The activation energy of this process is ~70 kcal/mol. Quantum chemical methods were employed to obtain data on possible intermediates in the processes studied and these results are used to interpret spectral and kinetic data.

INTRODUCTION

Compounds $R_2Si{=}O$ containing a silanone group (SG) were first stabilized using low-temperature matrix isolation techniques [1–3]. Early experiments showed that SGs are highly reactive (unlike carbonyl groups) and enter dimerization reactions at very low temperatures. Because isolation and stabilization of SG is difficult, experimental information on the mechanisms of SG reactions and quantitative data on the corresponding processes are rather scarce.

It was found in [4, 5] that the $(\equiv Si–O)_2Si{=}O$ groups may be stabilized on the surface of reactive silica. The high thermal stability and the accessibility to gas-phase molecules open broad avenues for the study of their reactivity. The interactions of $(\equiv Si–O)_2Si{=}O$ with H_2, CO_2, N_2O, and $HC{\equiv}CH$ were studied in [6, 7].

This work deals with experimental data on the direction and kinetics of SG reactions with a methane molecule and a methyl radical. To interpret spectral and kinetic data, we carried out quantum chemical calculations of the model systems.

METHODS

Experiments were carried out with samples of highly dispersed Aerosil A-300 in the form of semitransparent films, 50–100 μm thick. The preparation and activation procedures that make it possible to obtain a reactive silica (RSi) sample are analogous to those used earlier [8, 9].

The main type of diamagnetic defects on the RSi sample surface are silylene sites $(\equiv Si–O)_2Si{:}$ [5]. Their concentration is ~10^{13} cm^{-2}. To obtain SGs, silylene sites were oxidized by molecular oxygen [5]:

$$(\equiv Si–O)_2Si{:} + O_2 \longrightarrow (\equiv Si–O)_2Si{<}O_2 \qquad (I)$$

Then, dioxasilirane groups were transformed into the carbonate (300 K):

$$(\equiv Si–O)_2Si{<}O_2 + CO \longrightarrow (\equiv Si–O)_2Si{<}O_2{>}C{=}O, \qquad (II)$$

whose thermal decomposition at 550 K yields SG [4, 6]:

$$(\equiv Si–O)_2Si{<}O_2{>}C{=}O \longrightarrow (\equiv Si–O)_2Si{=}O + CO_2 \qquad (III)$$

Thus, one can quantitatively transform silylene sites into SGs.

A convenient method for SG registration is the optical method [6]. These sites are characterized by an absorption band with a maximum near 46000 cm^{-1} (5.6 eV). They can also be registered by IR spectroscopy using the band of $>Si{=}O$ bond stretching vibration (1307 cm^{-1} or its low-intensity overtone at 2605 cm^{-1}) [10].

In addition to diamagnetic sites, paramagnetic sites (PS) are stabilized on the surface of RSi; these are $(\equiv Si–O)_3Si^{\bullet}$ Their concentration is approximately two orders of magnitude lower. In the process of SG synthesis (reactions (I)–(III)), PSs quantitatively transform into peroxy radicals $(\equiv Si–O)_3Si–O–O^{\bullet}$ [11]. One can prepare a sample that contains only SGs. For that purpose, RSi was kept in an H_2 atmosphere (10^{-2} Torr) at 850 K. This method may help to transform the

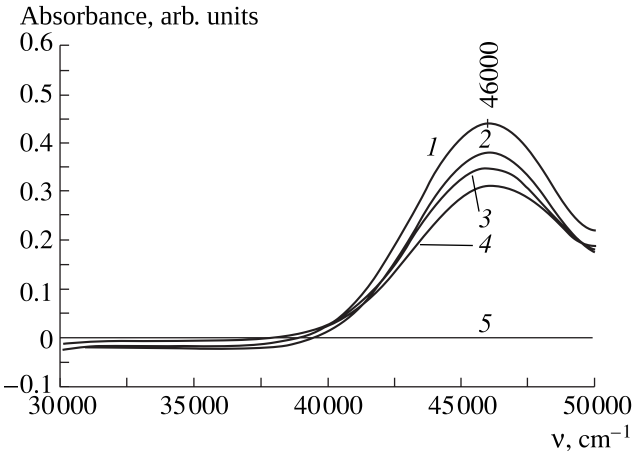

Fig. 1. Optical absorption spectra of silanone groups and their changes upon sample exposure to a methane atmosphere (P_{CH_4} = 54 Torr): (*1*) initial sample and upon keeping at 373 K for (*2*) 5, (*3*) 10, and (*4*) 15 min; (*5*) upon keeping at 473 K for 10 min.

$(Si–O)_3Si^{\bullet}$ radicals into the diamagnetic state $(\equiv Si–O)_3Si–H$ and obtain a sample containing only silylene sites (upon such a treatment their amount practically remains unchanged). Then, reactions (I) and (III) can produce silica with SGs on the surface and without PSs.

All experiments were carried out in high-vacuum conditions or in a controlled atmosphere. The pressure of gases in the system was measured using a Pirani gauge or a membrane gage (for pressures above 1 Torr).

Optical absorption spectra of the samples were recorded using a Specord-M40 spectrophotometer and IR spectra were recorded using a Digilab Bio-Rad FTS-7 Fourier-transform spectrometer (resolution, 2–4 cm^{-1}; 256 scans). For registration of spectra, the sample was transferred to a special part of a working cell. Measurements were carried out at room temperature.

Quantum chemical calculations were carried out using the Gaussian 94 program package [12]. In the calculations we used a fluorine-substituted molecular model of defects on the quartz surface, in which the ≡Si–O– groups are replaced by fluorine atoms. For instance, the $(\equiv Si–O–)_2Si(O^{\bullet})(CH_3)$ radical was a model of the $(F_2Si(O^{\bullet})(CH_3))$ radical. As was shown in [11], various types of paramagnetic and diamagnetic intrinsic and impurity defects of silica and their fluorine-substituted low-molecular analogs have similar physicochemical characteristics. The reasons for such a similarity are the spatial localization of electron states near a defect atom and the fact that a fluorine atom and a ≡Si–O– group have a similar substituent effect on the properties of a silicon atom that is bound to these groups.

The structure of molecules was optimized using the gradient approximation within the density functional theory (DFT in the B3LYP/6-311G(d,p) variant [13, 14]). For all optimized structures, we calculated their vibrational spectra. Transition states had a single negative eigenvalue of the Hessian matrix. The values of the reaction enthalpies at 0 K $\Delta H(0\text{ K}) = \Delta E(0\text{ K}) + \Delta(ZPE)$ (where $\Delta E(0\text{ K})$ is the difference between the full energies of the initial reactants and products and $\Delta(ZPE)$ is the zero-point energy) were calculated at the G2MP2//B3LYP/6-311G(d,p) level (the calculation scheme of the G2MP2 method [15] with the structure optimization and calculation of the vibrational spectrum at the B3LYP/6-311G(d,p) level). The G2 method was developed for calculating the heats of formation of compounds and usually describes the thermochemical characteristics of processes better than DFT. Energies were calculated using the formula

$$\begin{aligned} E(\mathrm{G2MP2(0K)}) = {} & E(\mathrm{QCISD(T,E4T)/6–311G(d,p)}) + (E(\mathrm{MP2/6–311 + G(3df,2p)}) \\ & - E(\mathrm{MP2/6–311G(d,p)})) + ZPE - 0.005n(\beta) - 0.0009(n(\alpha) - n(\beta)). \end{aligned} \tag{1}$$

The first term in this expression is the energy of the structure at the QCISD(T,E4T)/6-311G(d,p) level [12]; the second term is the change in the system energy with an increase the size of the basis set (the second parenthesis), the third term is the zero-point energy calculated at the DFT(B3LYP/6-311G(d,p)) level, and the rest of the terms are the semiempirical higher-level correction [15], in which $n(\beta)$ is the number of β electrons in the system, and $(n(\alpha) - n(\beta))$ is the difference between the number of α and β electrons.

RESULTS AND DISCUSSION

1. SG Methylation

Experiments on SG methylation were carried out using a sample that did not contain PSs (they were passivated by the preliminary treatment of RSi in an H_2 atmosphere; see the section on methods). Figure 1 shows a change in the spectrum of the optical absorption of such a sample upon its exposure to a methane atmosphere (initially at 373 K and then at 473 K, P_{CH_4} = 54 Torr). The IR spectrum also changes in the course of the process (Fig. 2). A decrease in the concentration of SGs is accompanied by the appearance and intensity growth of two new absorption bands: one is in the region of C–H stretching vibrations with a maximum at 2986 cm^{-1} and the other is in the region of O–H stretching vibrations at 3739 cm^{-1}. These changes are associated with the reaction

$$(\equiv Si–O)_2Si{=}O_2 + CH_4 \longrightarrow (\equiv Si–O)_2Si(OH)(CH_3) \quad \text{(IV)}$$

The structure of the product was confirmed by IR spectroscopic data. For the terminal hydroxy groups $(\equiv Si–O)_3Si(OH)$, the frequency of O–H stretching vibrations is 3749 cm^{-1} [8], which is higher than the registered value (3739 cm^{-1}). On the other hand, the frequency of C–H bond vibration (2986 cm^{-1}) is higher than the C–H bond stretching frequency in the $(\equiv Si–O)_2Si(H)CH_3$ group (2978 cm^{-1}) [16]. The shifts in the vibration frequencies observed can be associated with the difference in the structures of the silicon atom coordination spheres in the composition of the groups under consideration. This is also evident from the results of quantum chemical calculations of the vibrational spectra of the molecular models of surface groups $F_3Si(OH)$ (**I**), $F_2Si(OH)(CH_3)$ (**II**), and $F_2Si(H)(CH_3)$ (**III**). The frequencies of vibrations calculated at the DFT level were 3916 (131) and 3900 (101) cm^{-1} for the O–H bonds in molecules **I** and **II**; 3045 (0.1), 3121 (3.6), 3121.5 (3.6) cm^{-1}, and 3034 (0.3), 3107 (5.7), 3111 (4.3) cm^{-1} for the C–H bonds in molecules **II** and **III** (the intensities are indicated in parentheses in km/mol). The calculated shifts in the frequencies are in acceptable agreement with the experimental data.

The IR spectrum of the product contained only one band of the C–H stretching vibration of the methyl group rather than three (which might correspond to the number of C–H bonds). According to the results of quantum chemical calculations of molecule **II**, the symmetric vibration has a low intensity, and the frequencies of two antisymmetrical vibrations have close values and are probably registered as a single band.

Figure 3 shows kinetic data on the decay of SGs (as determined from a change in the band of optical absorption) and the accumulation of the OH and CH_3 groups (as determined from the measurements of the intensities of IR bands) in the course of methylation. Thus, the rate constant of SG interaction with a methane molecule is

$$k\,(373\ \text{K}) = (0.8 \pm 0.4) \times 10^{-22}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

Assuming a value of the preexponential factor of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, we obtain the activation energy of this reaction: 16.6 kcal/mol.

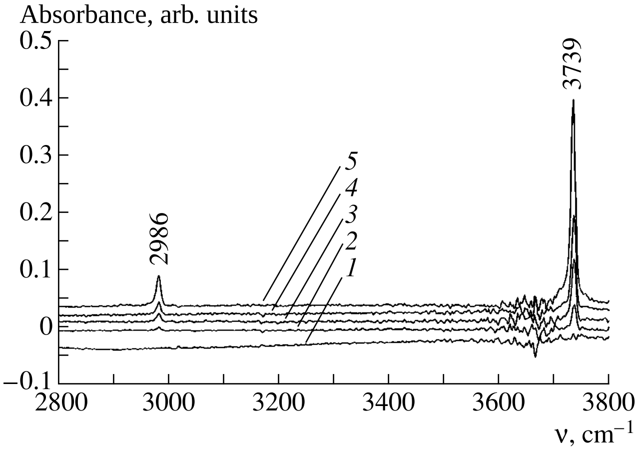

Fig. 2. IR spectra of the products of reaction of silanone sites with methane (P_{CH_4} = 54 Torr): (*1*) initial sample; (*2*) 5 min at 373 K; (*3*) 10 min at 373 K; (*4*) 15 min at 373 K; (*5*) 10 min at 473 K.

Figure 4 shows the structure of the transition state for the addition of methane molecule to a silanone group $F_2Si{=}O$. The activation energy and the enthalpy of this reaction at 0 K are

$$F_2Si{=}O + CH_4 \longrightarrow TS + 17.3\ \text{kcal/mol}$$

$$\longrightarrow F_2Si(OH)CH_3 - 52.1\ \text{kcal/mol}.$$

All energy characteristics of the model processes were calculated on the basis of the results presented in the table.

The calculated value of the activation energy agrees well with the experimental estimate. A high enthalpy value is notable for this reaction.

The above experimental and calculated data point to the fact that the methylation of silanone groups on the silica surface in the absence of paramagnetic sites occurs as a thermally activated molecular reaction (IV) with an activation energy of ~17 kcal/mol.

Radzig and Senchenya [6] experimentally studied the reaction of silanone group hydrogenation on the silica surface. The activation energy of the reaction

$$(\equiv Si–O)_2Si{=}O + H_2 \longrightarrow (\equiv Si–O)_2Si(OH)(H)$$

The values of *E*(G2MP2(0 K)) for individual compounds and transition states (TS) calculated using formula (1)

Compound	*E*(G2MP2(0 K)), atomic units	Compound	*E*(G2MP2(0 K)), atomic units
$F_2Si{=}O$	–563.83045	$F_2Si(O^{\bullet})(CH_3)$	–603.62422
CH_4	–40.40967	$F_2Si(OH)(^{\bullet}CH_2)$	–603.65987
$^{\bullet}CH_3$	–39.74391	$F_2Si{=}O\ldots{}^{\bullet}CH_3$ (TS)	–603.55621
$F_2Si{=}O\ldots CH_4$ (TS)	–604.21248	$F_2Si^{\bullet}–O–CH_3$	–603.62430
$F_2Si(OH)(CH_3)$	–604.32310		

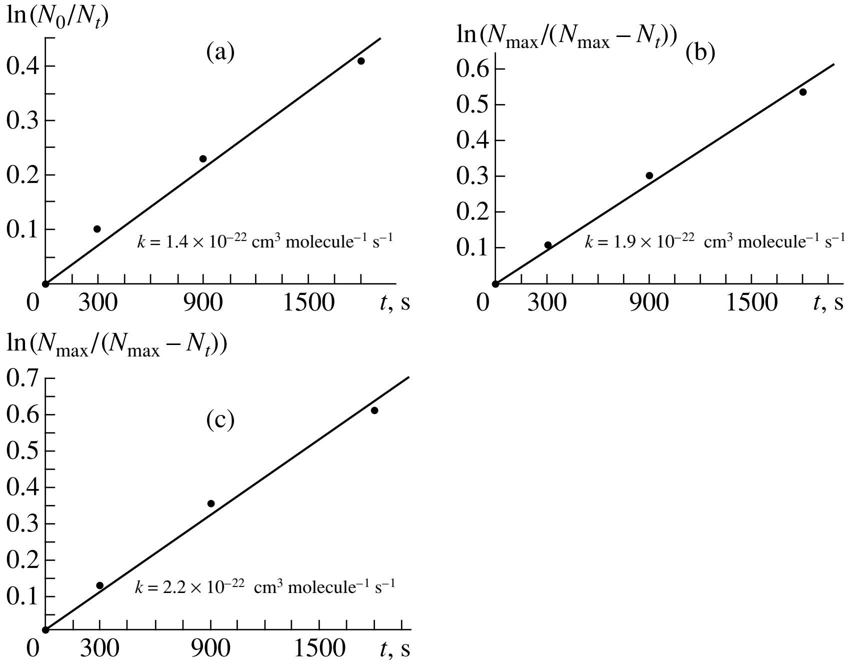

Fig. 3. Kinetic data on the decay of silanone groups and accumulation of CH_3- and OH groups for the reaction between silanone and methane (P_{CH_4} = 54 Torr; 373 K) obtained (a) from a change in the intensity of the band of optical absorption at 46000 cm^{-1} and from the growth of intensity of the IR band in the spectrum of (b) CH_3 groups (2986 cm^{-1}) and OH (c) groups (3739 cm^{-1}).

was 13.4 kcal/mol. Therefore, the reactivity of silanone groups toward hydrogen molecules is higher than toward methane molecules.

2. Thermal Decomposition of Silanone Group Methylation Product

The thermal decomposition of the $(\equiv Si–O)_2Si(OH)CH_3$ groups begins at temperatures above 750 K. Their initial amount in the sample was $16 \pm 0.5 \times 10^{18}$ g^{-1} (determined from the amount of chemisorbed methane molecules). After heating the sample for 10 min at 973 K, it evolved $7.0 \pm 0.2 \times 10^{18}$ CH_4 molecules, which is ~45% of the amount of CH_4 molecules chemisorbed by the sample. In the products of pyrolysis, a small amount of methanol was also found.

Figure 5 shows the IR spectrum of the sample upon pyrolysis. The intensities of the adsorption bands at 2986 and 3739 cm^{-1} decreased, pointing to the decay of a substantial portion of the $(\equiv Si–O)_2Si(OH)CH_3$ groups. Note also the form of the band in the region of O–H group stretching vibration. Along with a decrease in the intensity of the band at 3739 cm^{-1}, the bands of hydroxyl groups appeared at 3746 and 3749 cm^{-1}, which pointed to the formation of geminal ($(\equiv Si–O)_2Si(OH)(OH)$ and terminal ($(\equiv Si–O)_3Si(OH)$) groups [17]. The amount of $(\equiv Si–O)_2Si(OH)CH_3$ groups decomposed was determined from a change in the intensity of the band at 2986 cm^{-1} was ~70%.

Figure 6 shows the spectrum of optical absorption of the sample after pyrolysis (the SG band in the sample before methylation is shown for comparison). It can be seen that the intensity of silanone groups is partially restored. The distortion of the signal shape in the region of lower wavenumbers is due to the appearance of some silylene sites (the spectrum of optical absorption is shown in the figure by a dashed line). Their amount is at most 10% of the number of SGs formed. The degree of reduction of silanone groups determined from the above optical data was 42%.

Thus, experimental findings presented here suggest that the main channel for the thermal decomposition of the $(\equiv Si–O)_2Si(OH)CH_3$ groups is the reverse reaction of their formation (IV), the abstraction of a methane molecule:

$$(\equiv Si–O)_2Si(OH)(CH_3) \longrightarrow (\equiv Si–O)_2Si{=}O + CH_4 \quad \text{(V)}$$

However, this process is accompanied by other reactions as well. This is evident from the fact that the percentage of decomposed $(\equiv Si–O)_2Si(OH)CH_3$ groups determined by IR spectroscopy was higher than the amount of methane molecules and SGs formed. This was registered by monitoring the appearance of hydroxyl groups and silylene sites of the new types. The mechanism of these processes remains unclear so far. Note only that at the temperature of pyrolysis (973 K), the thermal decay of SGs is possible. Figure 7 shows the dependence of SG concentration on the temperature (determined from changes in the intensities of

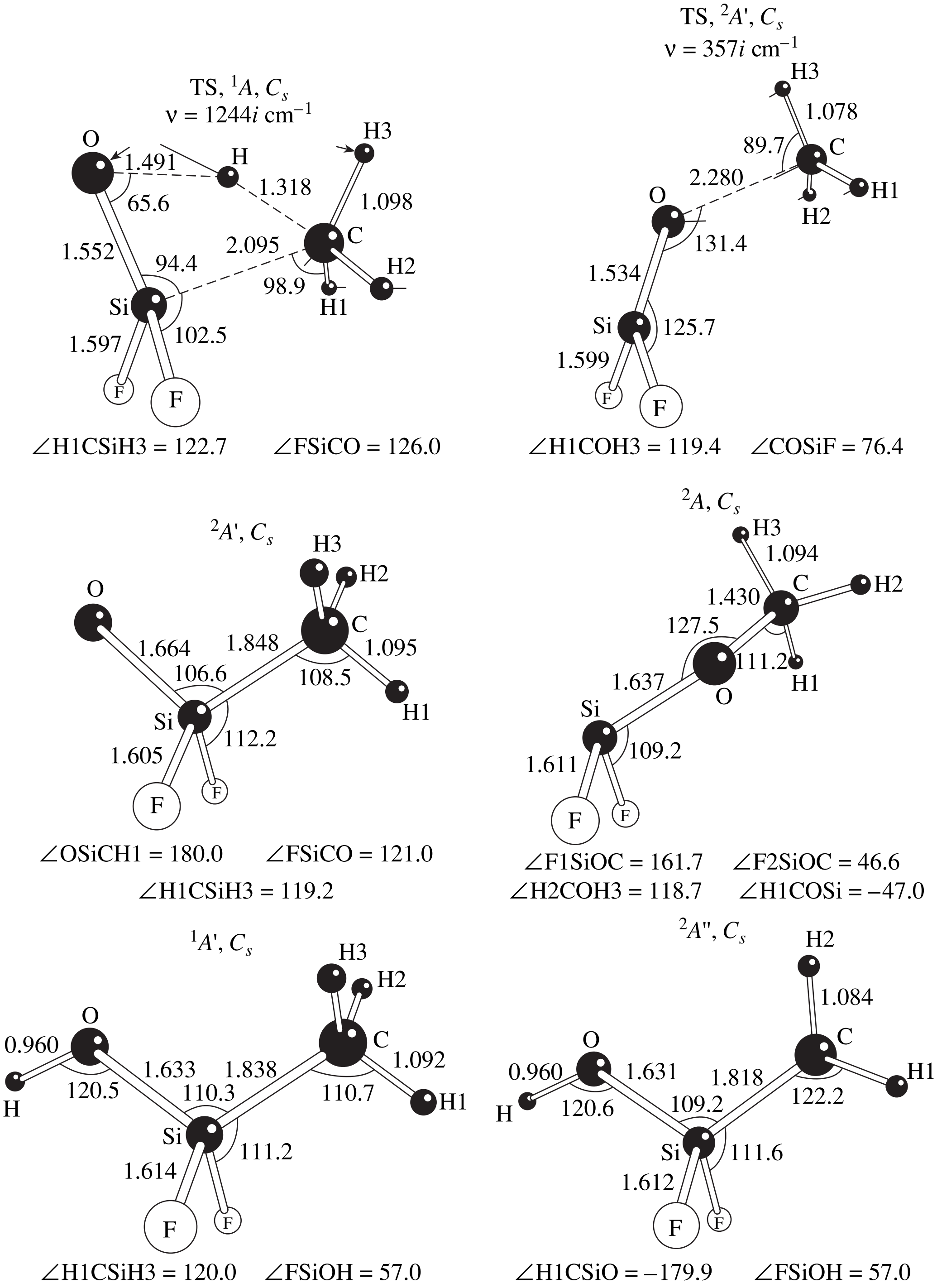

Fig. 4. Optimized structures of compounds and transition states (TS) and their symmetry types. For TS, the imaginary frequency of the motion along the reaction coordinate is shown. Arrows point to the directions of atomic shifts in a transition state.

their optical absorption band). Upon heating to 973 K, ~40% of the silanone sites decay.

According to the experimental data the degree of reaction (V) at 973 K (10 min) ranges from 0.45 (determined from desorption of methane molecules and SG reduction) to 0.7 (according to IR spectroscopic data). Therefore, the rate constant of reaction (V) is

$$k\ (973\ \text{K}) = (1\text{–}2) \times 10^{-3}\ \text{s}^{-1}.$$

If we assume the value of the preexponential factor 10^{12} s^{-1}, the activation energy of the reaction is 65–67 kcal/mol. The calculated activation energy for the

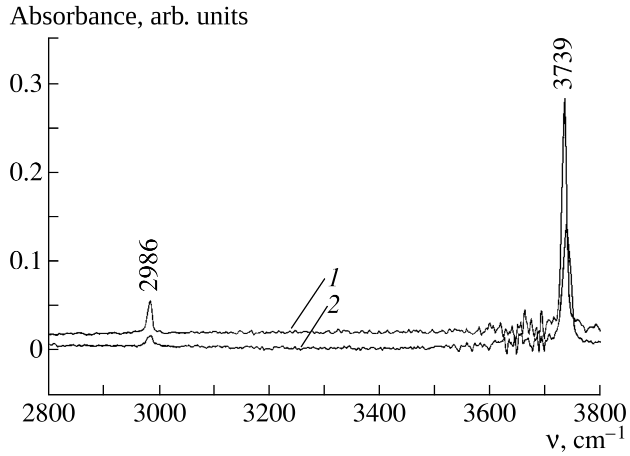

Fig. 5. (*1*) IR spectrum of the sample containing $(\equiv Si–O)_2Si(OH)(CH_3)$ groups and (*2*) the spectrum after their pyrolysis (10 min at 973 K).

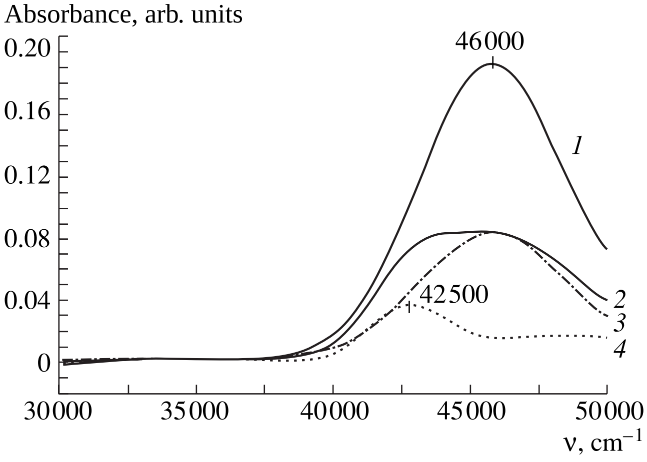

Fig. 6. Optical absorption spectra of (*1*) the sample with silanone groups; (*2*) methoxylated sample after pyrolysis for 10 min at 973 K; (*3, 4*) the result of spectrum *2* decomposition into the signals from silanone groups (*3*) and silylene groups (*4*).

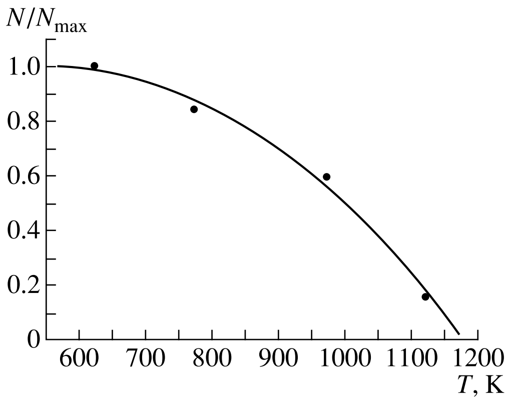

Fig. 7. Thermal stability of silanone groups (N/N_{max} is the relative concentration of SGs) (measurements using the optical method, exposure for 10 min at each temperature).

model process $F_2Si(OH)(CH_3) \longrightarrow F_2Si{=}O + CH_4$ is 69.4 kcal/mol. These two values agree with each other. The activation energy of decomposition of the $>Si(OH)(CH_3))$ group via the other channel with the abstraction of a methanol molecule and the formation of a silylene site calculated at the same theoretical level was noticeably higher:

$$F_2Si(OH)CH_3 \longrightarrow TS + 85.3\ \text{kcal/mol}$$

$$\longrightarrow F_2Si\!: + HOCH_3 + 65.1\ \text{kcal/mol}.$$

3. *Mechanism of Free Radical Methylation of Silanone Groups*

Silanone groups are efficient acceptors of low-molecular free radicals [4]:

$$(\equiv Si–O)_2Si{=}O + {}^{\bullet}H \longrightarrow (\equiv Si–O)_2Si^{\bullet}(OH).$$

It is this method that was used to apply the ESR method by introducing a paramagnetic label to identify the reaction product and the structure of the initial group and obtain the first experimental evidence for the stabilization of these diamagnetic sites on the surface of reactive silica.

The ${}^{\bullet}CH_3$ radical should participate in the free radical process of SG methylation. It was found in [4] that the methyl radical reaction with SG is

$$(\equiv Si–O)_2Si{=}O + {}^{\bullet}CH_3 \longrightarrow (\equiv Si–O)_2Si(OH)({}^{\bullet}CH_2)\ \text{(VI)}$$

The source of methyl radicals was the reaction

$$(\equiv Si–O)_3Si–O^{\bullet} + CH_4 \longrightarrow (\equiv Si–O)_3Si–OH + {}^{\bullet}CH_3$$

The reaction was carried out at 300 K and a low methane pressure. However, the mechanism of product formation in this reaction remains unclear. The formation of the $(\equiv Si–O)_2Si(OH)({}^{\bullet}CH_2)$ radical may occur either in the reaction of SG with a methyl radical via a synchronous mechanism with the simultaneous formation of the Si–C and O–H bonds or as two consecutive acts:

$$(\equiv Si–O)_2Si{=}O + {}^{\bullet}CH_3$$

$$\longrightarrow (\equiv Si–O)_2Si(O^{\bullet})(CH_3)$$

$$\longrightarrow (\equiv Si–O)_2Si(OH)({}^{\bullet}CH_2)$$

The second step of this process is the reaction of hydrogen atom transfer in the oxysilyl radicals $(\equiv Si–O)_2(O^{\bullet})(R)$ (R = H, D, CH_3, C_2H_5), which was studied in [18]. Oxy radicals were obtained by the photolysis of their precursors, $(\equiv Si–O)_2Si(NNO^{\bullet})(R)$. It was found that, for R=CH_3, the reaction of hydrogen atom transfer has an activation energy of ~16 kcal/mol and the process occurs via the classical (over-the-barrier) mechanism.

This means that in the case of the stepwise mechanism of reaction (VI) at low temperatures, the addition of the methyl radical to SG should result in the formation of the stable oxy radical at these temperatures. On the other hand, silyl oxy radicals are active in the reactions of hydrogen abstraction from hydrocarbon molecules, including CH_4. This reaction occurs at a temperature as low as 77 K, and its activation energy is close to zero. Therefore, at low temperatures one can expect the free radical methylation of SGs.

To check this hypothesis, we prepared a silica sample whose surface contained SGs (1.6×10^{19} g^{-1}) and oxy radicals $(\equiv Si–O)_3Si–O^\bullet$. With this purpose, the RSi sample was treated in an O_2 atmosphere at T = 873 K. Under these conditions, SGs and oxy radicals $(\equiv Si–O)_3Si–O^\bullet$ (6×10^{17} g^{-1}) [19] are stabilized on the surface. The amount of SGs and oxy radicals was determined by the volumetric method from the value of chemisorption of CO_2 and CO molecules [4]:

$$(\equiv Si–O)_2Si{=}O + CO_2 \longrightarrow (\equiv Si–O)_2Si\langle O_2 \rangle C{=}O;$$

$$(\equiv Si–O)_3Si–O^\bullet + CO \longrightarrow (\equiv Si–O)_3Si–O–{}^\bullet C{=}O$$

When this sample is in contact with methane (165 K, $P_{CH_4} = 10^{-2}$ Torr), methane rapidly chemisorbs on the surface and its rate is controlled by the diffusion of methane molecules. The amount of chemisorbed molecules coincides with the number of SGs within the accuracy of the volumetric measurements. The process ends with the complete decay of the SGs in the sample (the disappearance of the optical absorption band CH_4 at 46000 cm^{-1} (5.6 eV)) and the appearance of IR bands of stretching O–H and C–H vibrations at 3736 and 2984 cm^{-1}. The latter are close in their position and intensity ratios to those observed in the methylation of SGs (see above).

Experimental data presented above suggest that the process studied here is a free radical chain reaction. The initiation step is the reaction of the methane molecule with the oxy radical:

$$(\equiv Si–O)_3Si–O^\bullet + CH_4 \longrightarrow (\equiv Si–O)_3Si–OH + {}^\bullet CH_3$$

The methyl radical formed adds to a silicon atom in SG:

$$(\equiv Si–O)_2Si{=}O + {}^\bullet CH_3 \longrightarrow (\equiv Si–O)_2Si(O^\bullet)(CH_3),$$

and another oxy radical is formed, which continues the chain. The formation of radical $(\equiv Si–O)_2Si(OH)({}^\bullet CH_2)$ in this reaction would result in process termination. The reactivity of this radical at low temperatures is insufficient for free radical chain propagation. Bobyshev *et al.* [20] measured the rate constant of a similar reaction: $(\equiv Si–O)_3Si({}^\bullet CH_2) + CH_4 \longrightarrow (\equiv Si–O)_3Si(CH_3) + {}^\bullet CH_3$. Its value at 295 K is 4.1×10^{-22} cm^3 $molecule^{-1}$ s^{-1}. This allows us to estimate the activation energy of this reaction: 12.7 kcal/mol (the value of the preexponential factor is assumed to be equal to 10^{-12} cm^3 $molecule^{-1}$ s^{-1}).

If there were no step of chain branching, radical decay via recombination would retard the process. Because almost all SGs in the course of experiments with the molecules of methane reacted and because their concentration was more than an order of magnitude higher than the concentration of oxy radicals, we conclude that the SGs are very efficient radical acceptors since reactions between radicals usually occur with rate constants that are close to the gas-kinetic ones.

The low-temperature methylation of SGs is one of the limiting regimes of free-radical process occurrence. Another limiting regime corresponds to high temperatures and low methane pressures where oxy radicals have enough time to isomerize into an low-reactive radical form $(\equiv Si–O)_2Si(OH)({}^\bullet CH_2)$. In that case the activation energy of chain propagation would be ~13 kcal/mol (see above). The activation energy of the molecular reaction (IV) is ~17 kcal/mol. When the concentration ratio of PSs and SGs is 10^{-2} and the temperature is 450 K, the rates of the free radical and molecular channels of SG methylation become comparable.

We have not managed to experimentally register the product corresponding to methyl radical addition to the oxygen atom in SG:

$$(\equiv Si–O)_2Si{=}O + {}^\bullet CH_3 \longrightarrow (\equiv Si–O)_2Si^\bullet–O–CH_3,$$

although it was expected (quantum chemical data presented below support this) that such a process is thermochemically vary favorable.

The scheme below presents the results of quantum chemical calculations of energetics for two processes (methyl radical addition to a silicon atom and to an oxygen atom of SG in the $F_2Si{=}O$ molecule, which is the model of a surface site) (TS is the transition state):

$$1)\ F_2Si{=}O + {}^\bullet CH_3 \longrightarrow TS < 1\ kcal/mol$$
$$\longrightarrow F_2Si(O^\bullet)(CH_3) - 35.2\ kcal/mol$$
$$\longrightarrow F_2Si(OH)({}^\bullet CH_2) - 55.3\ kcal/mol;$$

$$2)\ F_2Si{=}O + {}^\bullet CH_3 \longrightarrow TS + 11.4\ kcal/mol$$
$$\longrightarrow F_2Si^\bullet–O–CH_3 - 31.3\ kcal/mol.$$

We failed to localize TS state corresponding to the addition of a methyl radical to a silicon atom. An increase in the distance between silicon atoms and carbon to 0.47 nm was accompanied by a monotonic increase in the energy of the system. That is, the activation energy of these reactions channel was at most 1 kcal/mol. The scheme presents the values of enthalpies of this reaction and oxy radical isomerization.

Figure 4 shows the structure of the TS for the reaction of methyl radical addition to the oxygen atom of SG. The calculated values of the activation energy and the thermal effect of this reaction channel are shown in the scheme. Thus, whereas the enthalpies are close for the addition of methyl radical to the oxygen atom in SG, it is necessary to overcome an activation barrier of ~11 kcal/mol. In the methyl radical, the carbon atom is negatively charged and one can assume that a portion of the activation barrier is due to the repulsion of similarly charged oxygen and carbon atoms. As a result, the predominant direction of the process is methyl radical addition to the silicon atom in SG.

ACKNOWLEDGMENTS

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