

Mechanisms of Heterogeneous Processes in the System $\text{SiO}_2 + \text{CH}_4$:

I. Methane Chemisorption on a Reactive Silica Surface

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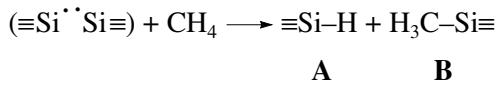
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Abstract—Experimental and quantum chemical study of reactive silica surface methylation is carried out. The main product of the reaction is the $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})(\text{CH}_3)$ groups, which are formed via a radical-chain process with the participation of methane molecules and paramagnetic and diamagnetic defects on the oxide surface. Spectral (optical and IR) characteristics of the groups participating in the process $(\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot}-\text{CH}_3$, $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})(\text{CH}_3)$, and $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{CH}_3)(\text{CH}_3)$ are determined. Information on the kinetics of separate steps of the process is obtained including rate constants and the activation energies of steps.

INTRODUCTION

Morterra and Low [1, 2] proposed a method for silica treatment resulting in a drastic increase in its chemisorption ability. The resulting material was called reactive silica (RSi). One of the systems reported in those papers was $\text{RSi} + \text{CH}_4$. IR spectroscopy helped determine that a reaction occurs in this system that is accompanied by the appearance of absorption bands at 2212 cm^{-1} (the region of Si–H stretching vibrations) and 2978 cm^{-1} (the region of C–H stretching vibrations) [2]. The authors assumed that the chemisorption sites on the RSi surface are $\equiv\text{Si}^{\cdot\cdot}\text{Si}\equiv$ groups in which two surface silica atoms are near each other, at a distance of several angstroms. Therefore, the following scheme for the formation of reaction products was proposed:



In agreement with this scheme, the above absorption bands were assigned to groups A and B formed via the dissociative chemisorption of methane molecules.

In more recent papers [3, 4], the structure of active chemisorption sites on the RSi surface was proposed. According to [3, 4], sites of two types are stabilized on the RSi surface: paramagnetic sites (PSs) consisting of the radical $(\equiv\text{Si}-\text{O})_3\text{Si}^{\cdot}$, which were discussed in [1, 2], and diamagnetic sites of the silylene type $(\equiv\text{Si}-\text{O})_2\text{Si}$, which contain dicoordinated silicon atoms rather than $\equiv\text{Si}^{\cdot\cdot}\text{Si}\equiv$ groups, as was proposed in [2]. The concentration of silylene-type sites (SSs) is 100 times higher than the concentration of paramagnetic sites. In this work, we continue the study of the $\text{RSi} + \text{CH}_4$ system that had begun from the work published in [2]. Heterogeneous processes with the participation of methane

molecules, which is the main component of natural gas, attract considerable attention because of the problem of its conversion [5]. Silica is often used as a catalyst support. The main attention in this work is given to the mechanistic study of reactions occurring in the system: elucidating the role of silica surface sites of various types, determining the nature of intermediate products formed in the course of the reaction, obtaining information on their spectral characteristics, and characterizing qualitatively their reactivity (kinetic data). The experimental part of this work is carried out using ESR, IR, and optical spectroscopy in the UV region. To interpret spectral and kinetic data, a quantum chemical study of the model systems is carried out.

METHODS

In the experiments, we used semitransparent films of pressed highly dispersed Aerosil A-300 (the initial specific surface area was $\sim 300 \text{ m}^2/\text{g}$). The films were $50\text{--}150 \mu\text{m}$ thick. The use of such samples made it possible to carry out quantitative spectral measurements in the IR and UV regions [6]. The procedure of thermochemical activation of silica surface resulting in the formation of reactive silica is described in detail in [2, 3, 6]. The concentration of paramagnetic sites $((\equiv\text{Si}-\text{O})_3\text{Si}^{\cdot})$ on the surface of an activated sample was $\sim 0.3 \times 10^{12} \text{ cm}^{-2}$ (or $\sim 2 \times 10^{18} \text{ g}^{-1}$, whereas the concentration of diamagnetic silylene sites containing a dicoordinated silicon atom $((\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot})$ was almost 100 times higher [3, 4]. The treatment of an RSi sample in an H_2 atmosphere (10^{-2} Torr) at 850 K makes it possible to transform radical $(\equiv\text{Si}-\text{O})_3\text{Si}^{\cdot}$ into the diamagnetic form $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{H}$. Thus, one can prepare an RSi sample on the surface of which there are only diamagnetic silylene sites (their number practically remains constant in the course of treatment).

All experiments were carried out under conditions of high vacuum or in a controlled atmosphere of various gases. The pressure of gases (CH_4 and O_2) in the system was measured using a Pirani gauge or a membrane gauge (when the pressure was higher than 1 Torr).

The optical absorption spectra of samples were recorded using a Specord-M40 spectrophotometer. IR spectra were recorded using a Digilab Bio-Rad FTS-7 Fourier-transform spectrometer (resolution, 2–4 cm^{-1} ; the number of scans, 256). Measurements were carried out at room temperature.

Quantum chemical calculations were carried out using the Gaussian 94 program package [7]. In the calculations, we used fluorine-substituted molecular models of defects of silica in which the $\equiv\text{Si}-\text{O}-$ groups are replaced by fluorine atoms. For instance, the $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ radical is modeled by the $\text{F}_2\text{Si}^\cdot-\text{CH}_3$ radical. It was shown in [8] that various types of paramagnetic and diamagnetic proper and admixture defects of silica and their fluorine substituted low-molecular analogs have close physicochemical characteristics. The reasons for such a similarity is the spatial localization of electron states near a defect atom and the fact that a fluorine atom and the $\equiv\text{Si}-\text{O}-$ group have a similar effect on adjacent silicon atoms.

Molecular structures were optimized using the gradient approximation within density functional theory (DFT) at the B3LYP/6-311G(d,p) level [9, 10]. For all optimized structures, the frequencies of stretching vibrations were calculated. The 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 initial reactants and products and $\Delta(ZPE)$ is the difference in the respective zero-point energies), were calculated at the G2MP2/B3LYP/6-311G(d,p) level (the calculation scheme of the G2MP2 method [11] with structure optimization and spectra simulation by the B3LYP/6-311G(d,p) method). The G2 method has been developed for calculating the heats of formation of compounds and is usually more suitable than DFT in characterizing the thermochemistry of a process. The enthalpies of compounds at 0 K were calculated using the formula

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

The first term in this expression is the energy of a structure at the QCISD(T,E4T)/6-311G(d,p) level [7]; the second term is the change in the system energy when the basis set is enlarged (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 a semiempirical higher-level correction [11]

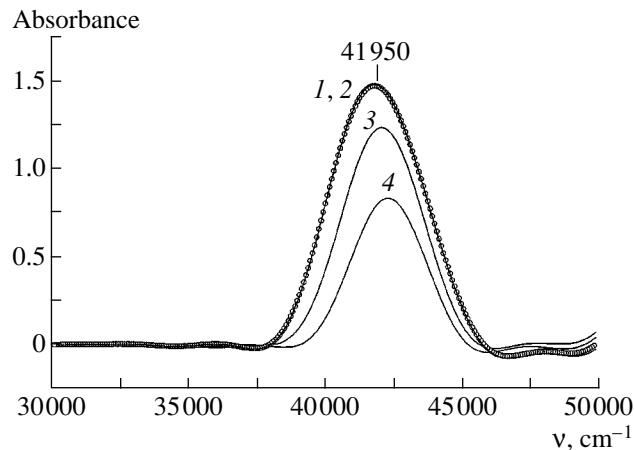


Fig. 1. Optical absorption spectra of the RSi sample: (1) initial; (2) after storing in a methane atmosphere for 20 min at 573 K (paramagnetic sites are passivated by pretreatment in H_2); (3) after storing in methane for 10 min at 523 K; and (4) after storing in methane for 10 min at 623 K (samples 3 and 4 contained paramagnetic sites). $P_{\text{CH}_4} = 50$ Torr.

in which $n(\beta)$ is the number of β electrons in the system and $n(\alpha) - n(\beta)$ is the difference between α and β electrons.

RESULTS AND DISCUSSION

1. Methylation of the RSi Surface

Figure 1a shows the spectrum of optical absorption of an RSi sample. The band at $\sim 42000 \text{ cm}^{-1}$ belongs to a silylene site [3]. A sample with the same amount of silylene sites without paramagnetic sites was prepared by high-temperature treatment in an H_2 atmosphere (see the experimental section). If this sample was allowed to stay in a methane atmosphere ($P_{\text{CH}_4} = 50$ Torr) at 573 K for 20 min, the band corresponding to silylene sites did not change its intensity (Fig. 1, spectrum 2) and there were no changes in the IR spectrum of the sample. Thus, under experimental conditions, silylene sites do not react with methane molecules.

The situation radically changes when the $(\equiv\text{Si}-\text{O})_3\text{Si}^\cdot$ radicals are also present on the RSi surface. Figure 1 (spectra 3, 4) show the spectra of optical absorption and Fig. 2 shows changes in the IR spectra of such a sample after storing in a methane atmosphere ($P_{\text{CH}_4} = 50$ Torr). Heating the sample in a methane atmosphere was accompanied by a decrease in the intensity of the bands of silylene site absorption and by the appearance of two new IR bands at 2212 cm^{-1} (in the region of Si–H stretching vibrations) and 2978 cm^{-1} (in the region of C–H stretching vibrations). The same IR bands were registered earlier in [2].

The ESR method was used at the initial stages of the process to show that there is a quantitative conversion

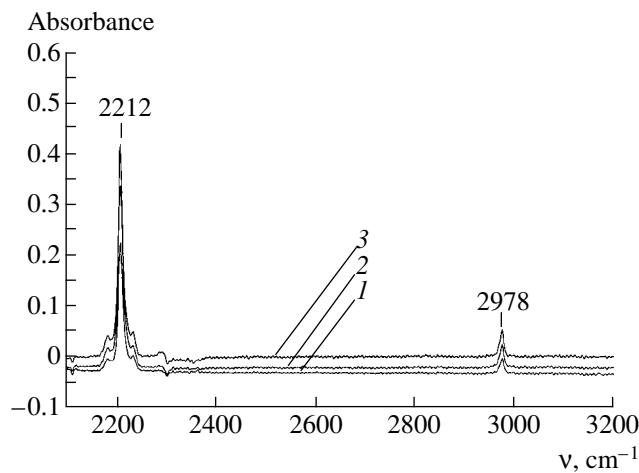
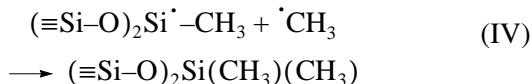
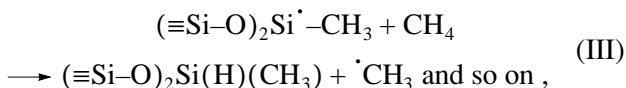
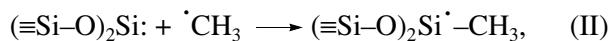
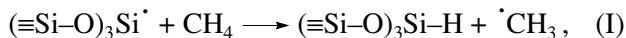


Fig. 2. IR spectra of the RSi sample upon exposure to methane ($P_{\text{CH}_4} = 50$ Torr, 10 min) at (1) 523, (2) 623, and (3) 773 K (the spectrum of the initial sample is subtracted).

of the $(\equiv\text{Si}-\text{O})_3\text{Si}^\cdot$ radicals into $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$. The latter were detected by ESR in [12]. They were obtained as a product of methyl radical addition to silylene sites when the following reaction served as a source of methyl radicals:



Because the concentration of paramagnetic sites was about two orders of magnitude lower than the concentration of silylene sites, the fact that the concentration of silylene sites decreases more than two times points to the development of the process along the free-radical pathway:

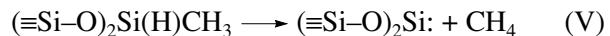


A silyl radical (reaction (I)) reacts with a methane molecule to form a methyl radical. The latter adds to the silylene site, which is an efficient acceptor of low-molecular free radicals [3, 4]. As a result, another silyl radical is formed, $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$, which further carries a free-radical chain (reactions (II)–(IV)). In contrast to [2], we associate the IR bands at 2212 and 2978 cm^{-1} with the $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})(\text{CH}_3)$ groups.

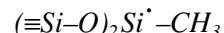
The absorption band with a maximum at 2212 cm^{-1} in the product of RSi methylation is due to the

stretching vibration of the Si–H bond in the $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})(\text{CH}_3)$ group. Earlier the bands of the Si–H stretching vibrations were detected on the silica surface that belong to fragments in which a silicon atom had other structures of the coordination sphere: $(\equiv\text{Si}-\text{O})_3\text{Si}(\text{H})$ (2299 cm^{-1}), $(\equiv\text{Si}-\text{O})_2(\text{H}-\text{O})\text{Si}(\text{H})$ (2270 cm^{-1}), and $(\equiv\text{Si}-\text{O})_2(\text{H})\text{Si}(\text{H})$ (2225 cm^{-1}) [13]. The appearance of the methyl group led to a further decrease in the frequency of the stretching Si–H vibration. According to the results of a DFT calculation, the frequencies of Si–H vibrations in the molecules F_3SiH , $\text{F}_2(\text{HO})\text{SiH}$, F_2HSiH , and $\text{F}_2(\text{CH}_3)\text{SiH}$ are 2376 , 2373 , 2302 , and 2287 cm^{-1} , respectively. Thus, we observed the same trend: a decrease in the frequency of the stretching vibration of the Si–H bond with a change in the chemical nature of a substituent at a silicon atom.

Groups formed in the course of RSi methylation $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})(\text{CH}_3)$ are thermally stable up to 800 K. A further increase in the temperature leads to their decay. Pyrolysis is accompanied by the reduction of the band of optical absorption of silylene sites and a synchronous decrease in the intensity of the IR bands at 2212 and 2978 cm^{-1} . In the course of pyrolysis, we detected the formation of gaseous products. The main low-molecular product of pyrolysis was methane (up to 90%), which was formed in amounts comparable with the number of methylated silylene sites. Experimental data suggest that the pyrolysis of the methylated sample occurs via the scheme

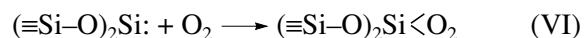


2. Spectral Characteristics of the Radicals



As shown in subsection 1, the $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ radical is a key intermediate in the process of RSi surface methylation. Here we present data on the optical and IR spectroscopic characteristics of paramagnetic sites. Data on their radiospectroscopic characteristics were obtained earlier [12].

The concentration of radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ formed by reactions (I) and (II) on the RSi surface enables its registration by ESR, but it was not sufficient to obtain data on its spectral characteristics in the IR and optical regions. To solve these problems, we prepared samples containing many more paramagnetic sites of the $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ type. With this purpose, a portion of silylene sites (up to 20%) was oxidized by molecular oxygen at 295 K [3, 4]:



The extent of the reaction was controlled by the optical method by monitoring a decrease in the intensity of the silylene site absorption band (see Fig. 1). It was found in [14] that dioxasilirane groups $(\equiv\text{Si}-\text{O})_2\text{Si} < \text{O}_2$ (DOSG) react with methane molecules

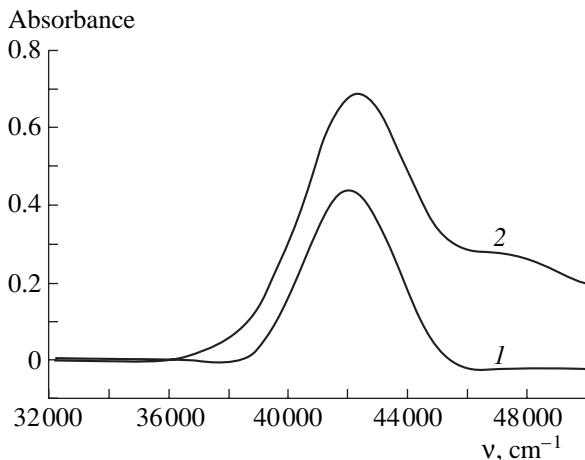
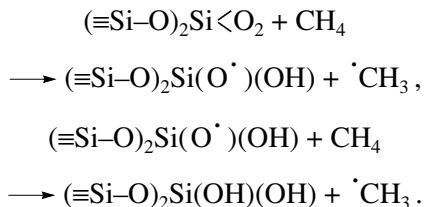


Fig. 3. Optical absorption spectrum of the partially oxidized RSi sample (1) before and (2) after exposure to methane ($P_{\text{CH}_4} = 10 \text{ Torr}$, 295 K, 15 min).

at room temperature. Methyl radicals are the products of this reaction:



The rate of the process is controlled by the first reaction. Methyl radicals formed react with silylene sites (see reaction (II)) with the formation of the required paramagnetic sites $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$.

The reaction of DOSG with methane occurred at 295 K and a pressure of $\sim 10 \text{ Torr}$. The rate constant of this reaction at 295 K is $(2.7 \pm 0.3) \times 10^{-20} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ [14] and the process is completed within tens of minutes. Under these conditions (temperature and gas pressure), methane molecules do not react with silyl radicals (see below). As a result, this expedient enabled an increase in the $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ concentration on the sample surface of more than ten times.

At a high concentration of radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$, one should also take into account the possibility of their decay in the reaction with a methyl radical. Under these conditions, the reaction scheme can take the following form:

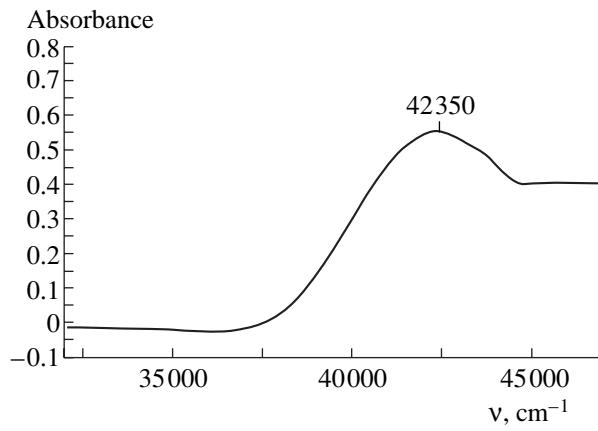
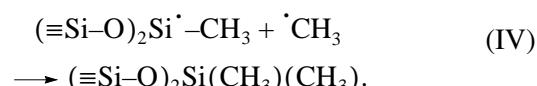
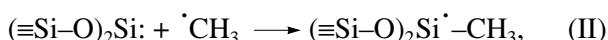
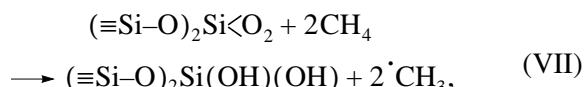
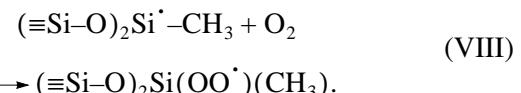


Fig. 4. Optical absorption spectrum of the $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ radical in the UV region.

2.1. The spectrum of optical absorption of the radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$. Figure 3 shows a change in the optical absorption spectrum of the partially oxidized sample in the process of its methylation. This change is due to a decrease in the concentration of silylene sites and an increase in the concentration of radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$. The spectrum of optical absorption of these paramagnetic sites is shown in Fig. 4.

Figure 5 shows a change in the optical density of the sample at a wavelength of 215 nm (46500 cm^{-1}) in the process of methylation of the partially oxidized RSi sample. This change is due to an increase in the concentration of radicals: at this wavelength the spectrum of optical absorption of the radical is rather intense (see Fig. 4) and it does not overlap with the spectrum of silylene site optical absorption. The concentration of radicals in the sample was determined by the volumetric method by measuring the amount of oxygen molecules needed for oxidation. As this takes place, silyl radicals transform into peroxide ones [15]:



Oxidation was carried out at room temperature and low oxygen pressure ($\text{O}_2 = 10^{-2} \text{ Torr}$). This prevented the oxidation of silylene sites present in the system.

The maximum of the band of optical absorption of the paramagnetic site $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ is near 4235 cm^{-1} (5.2 eV), that is in about the same region as that of the radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{H}$ [15]. A characteristic feature of the spectrum is a rather intense wing extended toward vacuum UV. A similar feature has been noted for the optical absorption spectrum of the radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{H}$ [8]. The nature of this phenomenon remains unclear. Note also the high intensity of this

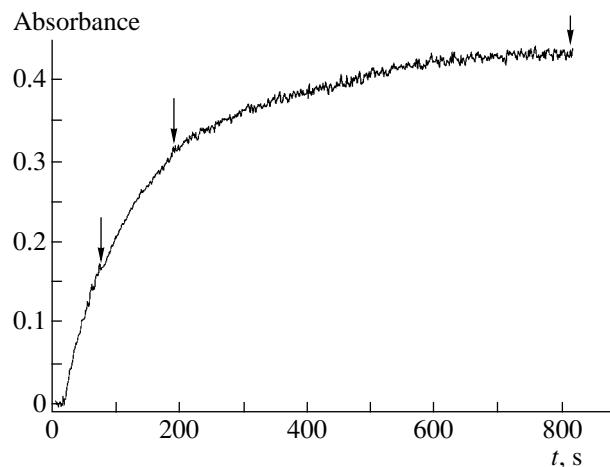


Fig. 5. The kinetic curve of $(\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot}-\text{CH}_3$ radical accumulation (dependence of the intensity of the band of optical absorption of the radical at a wavelength λ of 215 nm on the exposure time of the partially oxidized RSi sample in a methane atmosphere ($P_{\text{CH}_4} = 10$ Torr, 295 K). Arrows point to the moments of spectra recording.

optical absorption band which is typical of all silyl-type radicals.

2.2. Results of IR Spectroscopic Study. Figure 6 shows changes in the IR spectra in the process of methylation of a partially oxidized RSi sample. IR spectra were recorded at the points marked with arrows in Fig. 5 (for the time needed to record IR spectra, the reaction was interrupted by evacuating methane from the system). The reaction is accompanied by the appearance and growth of the intensity of the absorption band at 3746 cm^{-1} , which belongs to geminal hydroxy groups [15] (see reaction (VII)) and by the appearance of two bands in the region of C–H stretching vibrations at 2995 and 2976 cm^{-1} . We also registered the formation of low-intensity bands at 2859 , 2961 , and 2999 cm^{-1} , which belong to the stretching vibrations of C–H bonds

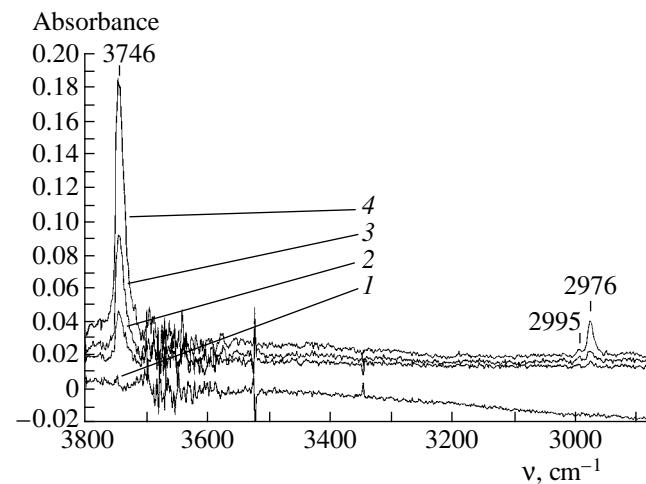


Fig. 6. IR spectra of the partially oxidized RSi sample in the process of methylation ($P_{\text{CH}_4} = 10$ Torr, 295 K) after (1) 0, (2) 80, (3) 200, and (4) 900 s.

in the $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{OH})(\text{OCH}_3)$ group [16]. This group is formed in a small amount via the addition of methyl radicals to DOSG [16]:

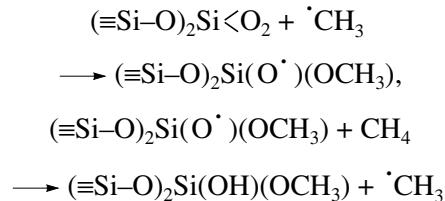


Table 1 shows the result of measurements of the amount of surface groups in the process of methylation (295 K, $P_{\text{CH}_4} = 10$ Torr) of the partially oxidized RSi sample. It can be seen from these data that the amount of paramagnetic sites $(\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot}-\text{CH}_3$ measured by

Table 1. Formation of products in the process of methylation (295 K, $P_{\text{CH}_4} = 10$ Torr) of the partially oxidized RSi sample

$[\text{>Si}(\text{OH})(\text{OH})] \times 10^{-18}, \text{g}^{-1}$	$[\text{PS}] \times 10^{-18}, \text{g}^{-1}$	$[\text{PS}]/[\text{PS}]_{\infty} (\text{IR})^*$	$[\text{>Si}(\text{CH}_3)(\text{CH}_3)] \times 10^{-18}, \text{g}^{-1}$	$[\text{>Si}(\text{CH}_3)(\text{CH}_3)]/[\text{>Si}(\text{CH}_3)(\text{CH}_3)]_{\infty} (\text{IR})^{**}$
0	0	0	0	0
2.24	3.04	0.33	1.44	0.12
5.1	5.74	0.67	4.46	0.33
10.2	8.2	1.0	12.2	1.0

Note: The initial amount of DOSG was $1.02 \times 10^{19}\text{ g}^{-1}$ according to volumetric measurements (reaction (VI)). The relative amount of $\text{>Si}(\text{OH})(\text{OH})$ groups was determined from the intensity of the bands at 3746 cm^{-1} , and their concentration was determined assuming $\Delta[\text{>Si}(\text{OH})(\text{OH})] = -\Delta[\text{DOSG}]$. The amount of paramagnetic sites $(\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot}-\text{CH}_3$ was determined from data on optical measurements (Fig. 5) with calibration according to the results of volumetric measurements (reaction (VIII)). The amount of $\text{>Si}(\text{CH}_3)(\text{CH}_3)$ was calculated from the condition of the material balance $[\text{>Si}(\text{CH}_3)(\text{CH}_3)] + 1/2 [\text{>Si}^{\cdot}-\text{CH}_3] = [\text{>Si}(\text{OH})(\text{OH})]$ in relative units.

* Results of IR measurements (rel. units) of absorption bands at 2995 cm^{-1} . ** At 2976 cm^{-1} .

Table 2. Kinetics of changes in the concentrations of various groups ($\times 10^{-18}$, g $^{-1}$) in the process of RSi sample methylation with an increased concentration of paramagnetic sites ($T = 393$ K, $P_{\text{CH}_4} = 45$ Torr)

No.	Time, s	[>Si:]	[>Si $^{\cdot}$ –CH $_3$]	[>Si(H)(CH $_3$)]	[>Si(CH $_3$)(CH $_3$)]
1	0	9.30	6.2	0	1.7
2	300	8.28	5.8	1.22	1.9
3	900	7.04	4.68	3.02	2.46
4	1800	5.44	3.4	5.26	3.1
5	3600	3.72	2	7.68	3.8
6*	∞	0	0	12.4	4.8

* The sample was heated in a methane atmosphere for 10 min at 473 K.

the optical method and the intensity of the band at 2995 cm $^{-1}$ are proportional to each other. The ratio of intensities of the bands at 2995 and 2976 cm $^{-1}$ is maximal at the initial stage of the process (see Table 1) when the contribution of reaction (IV) to the formation of products is not significant. This makes it possible to associate the band at 2995 cm $^{-1}$ with the stretching vibrations of the C–H bonds in the radical ($\equiv\text{Si}–\text{O}$) $_2\text{Si}^{\cdot}–\text{CH}_3$. Further evidence for the fact that this band belongs to the above-mentioned paramagnetic centers is that their oxidation (see reaction (VIII)) is accompanied by the shift of this band. Because of the low intensity, we were unable to determine the new position of the band. According to the results of quantum chemical calculation at the DFT level, the transition from the radical $\text{F}_2\text{Si}^{\cdot}–\text{CH}_3$ to the radical $\text{F}_2\text{Si}(\text{OO}^{\cdot})(\text{CH}_3)$ is accompanied by an increase in the frequencies of C–H stretching vibrations in the methyl group and by a decrease in their intensity (numbers in parentheses shows the values of band intensities in km/mol): {3029 (1.3); 3111 (3.4); and 3129 (3.4) cm $^{-1}$ } and {3048 (0.4); 3122 (1.2); and 3132 (0.3) cm $^{-1}$ }.

The band at 2976 cm $^{-1}$ is associated with the ($\equiv\text{Si}–\text{O}$) $_2\text{Si}(\text{CH}_3)(\text{CH}_3)$ groups. The intensity of this band noticeably increases at the last stage of the process when reaction (IV) begins to play a more important role due to an increase in the concentration of paramagnetic sites and a decrease in the concentration of silylene sites. In one of the experiments, we prepared an RSi sample in which a still greater portion of silylene sites (up to 60%) were oxidized. After carrying out the reaction of methane, the IR spectrum of the reaction products contained the absorption band belonging to geminal hydroxy groups and the band at 2976 cm $^{-1}$, whereas the band at 2995 cm $^{-1}$ was practically absent.

3. Kinetic and Thermochemical Characteristics of Reactions Studied

To determine the kinetic characteristics of the methylation process, we prepared a sample of partially oxidized RSi that was treated by methane at room tempera-

ture. As a result of reactions with methane molecules (see reactions (VII), (II), (IV)), DOSG transformed into geminal hydroxy groups, some portion of silylene sites remained, and the radical ($\equiv\text{Si}–\text{O}$) $_2\text{Si}^{\cdot}–\text{CH}_3$ and the product of methyl radical decay, ($\equiv\text{Si}–\text{O}$) $_2\text{Si}(\text{CH}_3)(\text{CH}_3)$, were formed. The first row in Table 2 shows the amount of these groups.

The methylation of the sample was carried out at 393 K and a methane pressure of 45 Torr. The concentrations of paramagnetic sites, silylene sites, and the products of their reactions with methane ($\equiv\text{Si}–\text{O}$) $_2\text{Si}(\text{OH})(\text{OH})$, ($\equiv\text{Si}–\text{O}$) $_2\text{Si}(\text{H})(\text{CH}_3)$, and ($\equiv\text{Si}–\text{O}$) $_2\text{Si}(\text{CH}_3)(\text{CH}_3)$) were traced using optical and IR spectroscopy. The values of [PS], [DOSG] $_0$, and [SS] $_0$ in the sample were determined by the volumetric method using the value of oxygen chemisorption on these sites (see reactions (VI), (VIII)). This made it possible to obtain data on the changes in the concentrations of the groups (Table 2) participating in the process using the conditions of material balance (see reactions (II), (IV), (VII)):

$$[>\text{Si}(\text{CH}_3)(\text{CH}_3)] + 1/2[>\text{Si}^{\cdot}–\text{CH}_3] = [\text{DOSG}],$$

$$[\text{SS}]_0 = [>\text{Si}(\text{CH}_3)(\text{CH}_3)]_\infty + [>\text{Si}(\text{H})(\text{CH}_3)]_\infty.$$

For the process of RSi surface methylation described by reactions (II)–(IV), we obtained expressions that relate changes in the concentrations of separate intermediates and the products in the course of the process. The assumption that the process is at a steady state with respect to the methyl radical leads to the following expression of its concentration:

$$[\text{CH}_3]_{\text{st}} = k_3[\text{PS}][\text{CH}_4]/(k_2[\text{SS}] + k_4[\text{PS}]).$$

Changes in the concentrations of silylene and paramagnetic sites in the course of the process are related by the expression

$$\ln([\text{SS}]_0/[\text{SS}])/\ln([\text{PS}]_0/[\text{PS}]) = k_2/2k_4. \quad (2)$$

Therefore, one can determine the ratio of the rate constants of methyl radical addition to paramagnetic and silylene sites using formula (2) by controlling

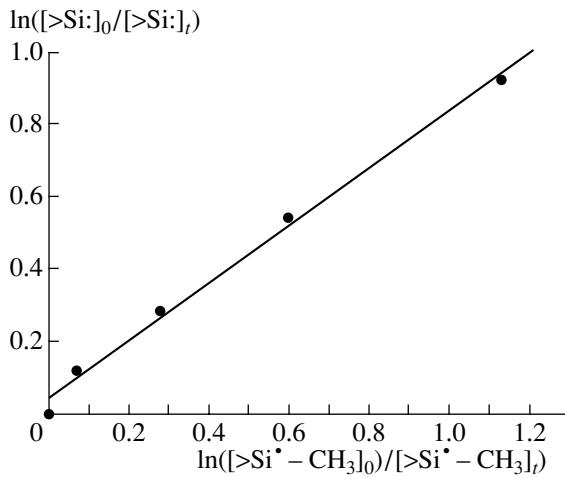


Fig. 7. Relationship between the concentrations of silylene sites and paramagnetic sites in the process RSi sample methylation ($P_{\text{CH}_4} = 45$ Torr, 393 K).

changes in the concentrations of paramagnetic and silylene sites in the sample in the course of methylation.

Figure 7 shows the relation of the concentrations of paramagnetic sites in the coordinates of Eq. (2) according to the data shown in Table 2. The slope of this line is 0.75 ± 0.1 . Therefore, $k_2 = (1.5 \pm 0.2)k_4$. Thus, these reactions have close values for the rate constants. The reactions of radical addition occur without an activation barrier. Therefore, the reaction of methyl radical addition to a silylene site also occurs without a barrier. The efficient addition of methyl radicals to silylene sites was observed at a temperature as low as 77 K [12]. A similar result was obtained for the ratio of the rate constants of H addition to the silylene site and the radical $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{H}$ [17]. We can assume that the absolute values of the rate constant is close to that observed in gas-phase kinetics, $10^{-11 \pm 1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The value of the constant k_3 can be determined from the rate of Si–H bond accumulation (Eq. (III))

$$d[\text{Si}-\text{H}]/dt = k_3[\text{PS}][\text{CH}_4].$$

Figure 8 illustrates the relationships between the values $d[\text{Si}-\text{H}]/dt$ (the result of graphical differentiation of data presented in Table 2) and $[\text{PS}]$ for the methylation process. The rate constant determined from the slope of this line was k_3 (393 K) = $(5.3 \pm 1) \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Assuming the normal value of the preexponential factor ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the activation energy of this bimolecular reaction is 16.7 kcal/mol.

Using the value of k_2 , one can estimate the rate of methylation of the RSi sample surface where the concentration of paramagnetic sites is two orders of magnitude lower,

$$-\Delta[\text{SS}]/\Delta t \approx k_3[\text{CH}_4]N_{\text{R}}.$$

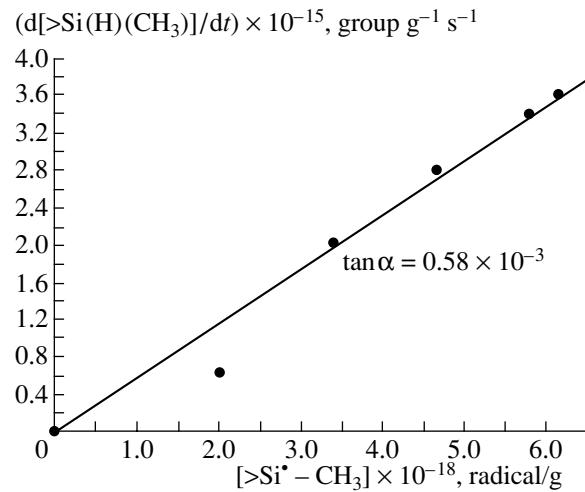


Fig. 8. Dependence of the rate of silane group formation on the concentration of paramagnetic sites in the process RSi sample methylation ($P_{\text{CH}_4} = 10$ Torr, 295 K).

Here N_{R} is the concentration of paramagnetic sites on the RSi surface and $[\text{CH}_4]$ is the concentration of methane molecules in the gas phase. At 523 K, the amount of silylene sites decreased by 30% (as determined from a change in the intensity of the silylene site optical absorption, Fig. 1, curve 3) for 10 min at $P_{\text{CH}_4} = 46$ Torr. The value of the rate constant of reaction (III) at 523 K is k_3 (523 K) = $1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (assuming that k_3 (393 K) = $5.3 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and that the activation energy is 16.7 kcal/mol (see above)). The concentration of paramagnetic sites was assumed to be equal to 1.5% of the concentration of silylene sites. As a result we obtain $\Delta[\text{>Si}]/\Delta t N_{\text{R}} = 0.11 \text{ s}^{-1}$ and $k_3[\text{CH}_4] = 0.08 \text{ s}^{-1}$. Thus, the above radical process indeed can maintain the rate of silylene site methylation.

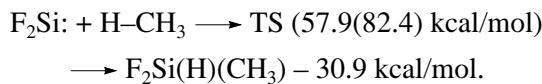
The pyrolysis of a methylated RSi sample is accompanied by the desorption of methane molecules from the sample surface and by the recovery of silylene sites. Figure 9 shows the kinetic curve of $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})\text{CH}_3$ decomposition at 973 K. The process kinetics were monitored by measuring the amount of methane molecules desorbed from the sample. The reaction occurs according to the first-order rate law with the rate constant of reaction (V)

$$k \text{ (973 K)} = (6.1 \pm 1) \times 10^{-4} \text{ s}^{-1},$$

as determined from the slope of a straight line. Assuming the normal value of the preexponential factor 10^{12} s^{-1} (10^{13} s^{-1}), we obtain that $E_a = 72$ (77) kcal/mol.

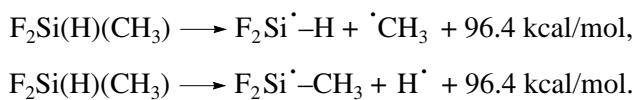
We carried out quantum chemical calculations of the energetics of formation and decomposition of $\text{>Si}(\text{H})\text{CH}_3$ groups. The F_2Si : molecule was used as a model of a silylene site (all calculations of energy char-

acteristics for the model processes were based on the results shown in Table 3):



The structures of two transition states for this reaction, which differed noticeably in energies and the structure of the reaction product ($\text{F}_2\text{Si}(\text{H})(\text{CH}_3)$), are shown in Fig. 10. Assuming that the enthalpy of reaction (V) is 31 kcal/mol (according to the calculation), the activation energy of silylene site insertion into a C–H bond of a methane molecule is $E = 72(77) - 31 = 41(46)$ kcal/mol. The calculated value is even higher: 58 kcal/mol. Note that calculations usually overestimate the values of activation barriers. Therefore, it becomes clear that silylene site methylation via the molecular mechanism (in the absence of paramagnetic sites) may only occur in very severe conditions.

The results of quantum chemical calculations of the enthalpies for other possible channels of $\text{>Si}(\text{H})(\text{CH}_3)$ group decomposition via the homolytic cleavage of Si–H or Si–C bonds are as follows:



The activation energies of these processes are close because the activation energies of the reverse reactions of radical recombination are equal to zero. Indeed, quantum chemical calculations showed that the corresponding transition states are characterized by the elongation of the bond cleaved (>0.35 nm). Thus, the molecular mechanism of $\text{>Si}(\text{H})(\text{CH}_3)$ group decomposition is preferable compared to the free-radical mechanism.

The free-radical methylation of the RSi sample surface begins with reaction (I) in which the $(\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot}$ radical takes part. The rate constant of the reaction of the $(\equiv\text{Si}-\text{O})_2(\text{H}-\text{O})\text{Si}^{\cdot}$ radical, which is close to the radical $(\equiv\text{Si}-\text{O})_3\text{Si}^{\cdot}$, with a methane molecule at 295 K was measured in [18] ($4.9 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Assuming a preexponential factor of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, we

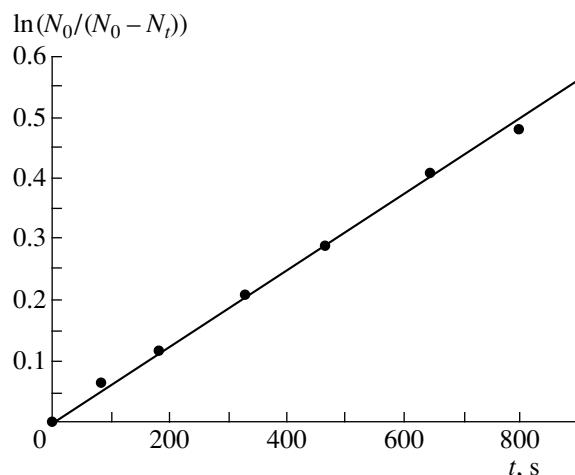


Fig. 9. Kinetic curve of $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{H})(\text{CH}_3)$ group decomposition at 973 K (according to the measurements of methane molecules evolved).

obtain the activation energy of this reaction: 13.9 kcal/mol (in [18] this was estimated as 12.8 kcal/mol assuming a value of the preexponential factor of $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Thus, the replacement of the oxygen atom by a methyl group in the coordination sphere of the silicon atom in a $(\equiv\text{Si}-\text{O})_2\text{Si}^{\cdot}-\text{CH}_3$ radical leads to a noticeable decrease in the reactivity.

This conclusion is supported by the results of quantum chemical calculations. Figure 10 shows the structures of transition states for hydrogen atom abstraction from a methane molecule by two silyl radicals $\text{F}_3\text{Si}^{\cdot}$ and $\text{F}_2\text{Si}^{\cdot}-\text{CH}_3$ with different structures of the coordination sphere.

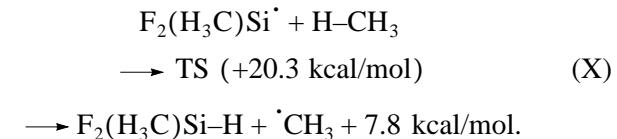
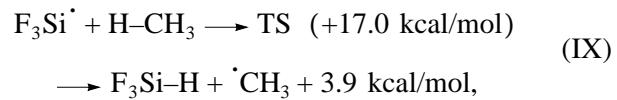


Table 3. The values of $E(\text{G2MP2}(0 \text{ K}))$ for individual compounds and transition states

Compound	$E(\text{G2MP2}(0 \text{ K}))$, at. units	Compound	$E(\text{G2MP2}(0 \text{ K}))$, at. units
$\cdot\text{H}$	-0.5	$\text{F}_2\text{Si}^{\cdot} \dots \text{CH}_4(\text{TS2})$	-528.93418
$\text{F}_2\text{Si:}$	-488.65583	$\text{F}_3\text{Si}^{\cdot}$	-588.44737
CH_4	-40.40967	F_3SiH	-589.10693
$\cdot\text{C H}_3$	-39.74391	$\text{F}_3\text{Si}^{\cdot} \dots \text{H}-\text{CH}_3(\text{TS})$	-628.83001
$\text{F}_2\text{Si}^{\cdot}-\text{CH}_3$	-528.46142	$\text{F}_2(\text{CH}_3)\text{Si}^{\cdot} \dots \text{H}-\text{CH}_3(\text{TS})$	-568.83878
$\text{F}_2\text{Si}(\text{H})(\text{CH}_3)$	-529.11473		
$\text{F}_2\text{Si:}\text{CH}_4(\text{TS1})$	-528.97326		

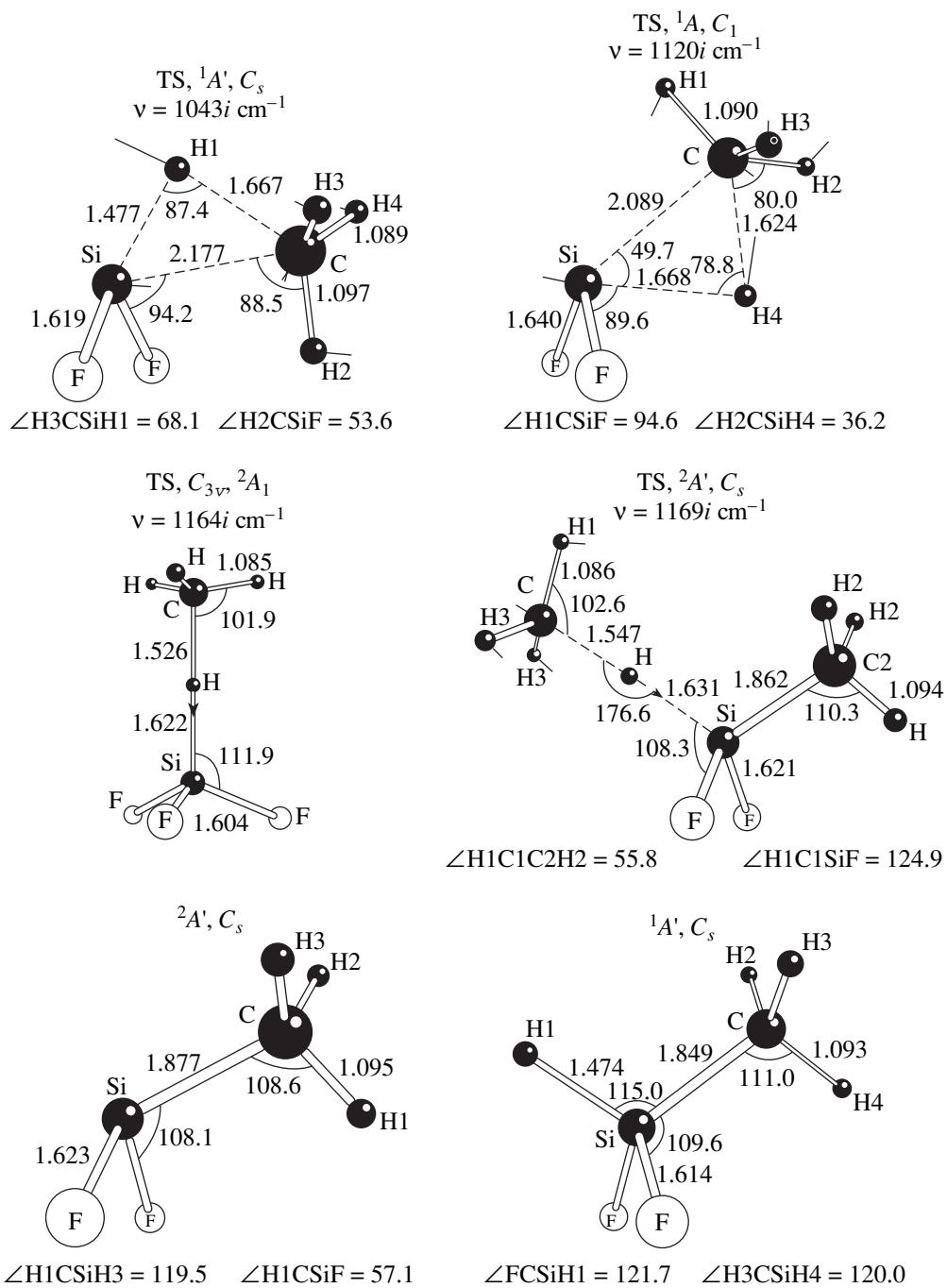
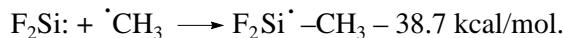


Fig. 10. Optimized structures of compounds and transition states (TS), symmetry types, and point groups. For TSs, the imaginary frequencies of moving along the reaction coordinates are presented. Arrows point to the directions of atomic shifts in the transition states.

According to the results of calculations, the activation energy of reaction (IX) is 3.3 kcal/mol lower than the activation energy of reaction (X), and the enthalpy is higher by 3.9 kcal/mol. Thus, the results of calculations also point to a decrease in the activation energy when the methyl group is replaced by a more electronegative substituent (in our case, a fluorine atom) at the silicon atom in the silyl radical. A stronger Si–H bond

is formed in the reaction product. In the F₃SiH molecule, the strength of the Si–H bond is ~100 kcal/mol [8], and the Si–H bond in the surface group (≡Si–O)₃SiH has a similar strength [8]. Proceeding from this information, we can estimate the strength of the Si–H bond in a F₃(H₃C)SiH molecule and in the (≡Si–O)₂Si(H)(CH₃) group as 96 kcal/mol.

The calculated value of the enthalpy of methyl radical addition to a silylene site is presented below:



We may assume that the enthalpy of methyl radical addition to the silylene site on the silica surface has a close value. Indeed, the enthalpy of the similar reaction of hydrogen atom addition to an $\text{F}_2\text{Si:}$ molecule (-38.5 kcal/mol) calculated at the G2MP2 level is close to the experimental value (-39 ± 2 kcal/mol) for the reaction of hydrogen atom to silylene site. The results obtained point to the relatively low thermal stability of the radical $>\text{Si}^\cdot - \text{CH}_3$. At a temperature as low as 600 K, the lifetime of this radical with respect to the unimolecular reaction of its decomposition with the abstraction of a methyl radical is ~ 1 min (the value of the preexponential factor in the rate law is assumed to be 10^{13} s^{-1} , and the activation energy of decomposition is ~ 39 kcal/mol). This means that, for the reaction of RSi methylation at elevated temperatures, one has to take into account the thermal decomposition of the $>\text{Si}^\cdot - \text{CH}_3$ radical. This should lead to an increase in the rate of paramagnetic site decay and to a decrease in the rate of methylation.

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