

Mechanisms of Heterogeneous Processes in the System $\text{SiO}_2 + \text{CH}_4$: III. Products of $>\text{Si}<\text{O}_2$ Group Methylation

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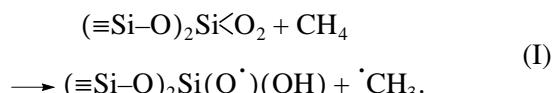
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Abstract—The methods of optical, ESR, and IR spectroscopy were used to obtain data on the structure and mechanism for the formation of the products in the reaction of dioxasilirane groups $(\equiv\text{Si}-\text{O})_2\text{Si}<\text{O}_2$ (DOSG) stabilized on the silica surface. Depending on the regime of the reaction (temperature and methane pressure), the process is accompanied by the formation of various products: methoxy ($-\text{O}-\text{CH}_3$) and ethoxy ($-\text{O}-\text{C}_2\text{H}_5$) groups. The process mechanism is elucidated: this is a free-radical reaction in which paramagnetic sites are generated in the reaction between DOSG and methane molecules. The formation of final products is due to the reactions $>\text{Si}(\text{O}^\cdot)(\text{OCH}_3) + \text{CH}_4 \longrightarrow >\text{Si}(\text{OH})(\text{OCH}_3) + \cdot\text{CH}_3$ and $>\text{Si}(\text{O}^\cdot\text{CH}_2)(\text{OH}) + \cdot\text{CH}_3 \longrightarrow >\text{Si}(\text{OH})(\text{OC}_2\text{H}_5)$. The ratio of the rate constants of methyl radical addition to $(\equiv\text{Si}-\text{O})_2\text{Si}$ and $(\equiv\text{Si}-\text{O})_2\text{Si}<\text{O}_2$ at room temperature was determined experimentally (4.6 ± 1.0).

INTRODUCTION

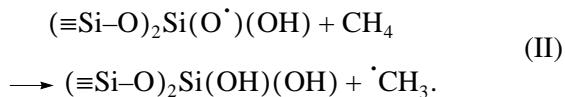
In the early 1970s, in the pioneering papers [1, 2] devoted to the development of the method of silica surface activation resulting in a drastic increase in its chemisorption activity (the preparation of reactive silica (RSi)), it was shown that methane chemisorbs on the oxygen-oxidized surface of RSi at room temperature. The authors showed the formation of a number of IR bands in the region of C–H stretching vibrations at 2800 – 3200 cm^{-1} , which belong to surface groups of two types: $-\text{OCH}_3$ and $-\text{OC}_2\text{H}_5$. However, according to [2], the mechanism of their formation remains unclear.

More recently, it was found [3, 4] that the high chemisorption activity of the RSi samples is due to the stabilization of sites on its surface that involve a two-coordinated silicon atom $(\equiv\text{Si}-\text{O})_2\text{Si}$: (SS). Oxidation by molecular oxygen transform them into dioxasilirane groups $(\equiv\text{Si}-\text{O})_2\text{Si}<\text{O}_2$ (DOSG). In this three-membered cycle, the bond between oxygen atoms is weakened. This leads to surprising chemical properties of these groups. Thus, at a temperature as low as room temperature, these groups react with methane molecules, and this reaction is accompanied by the formation of free radicals [5]:



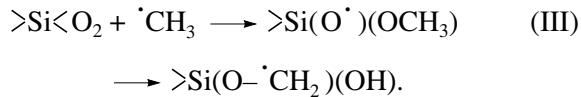
The rate constant of this reaction is $k = (2.2 \pm 0.5) \times 10^{-13} \exp(-(9.5 \pm 0.5) (\text{kcal/mol})/RT \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Oxysilyl radicals formed in this reaction are highly reactive in the reactions of hydrogen atom abstraction:



The activation energy of reaction (II) is close to zero.

According to [5, 6], the addition of the methyl radical to DOSG occurs via the following scheme:



The final product of this reaction was experimentally registered by the ESR method. The formation of an intermediate product was only suggested.

Taking into account information on the structure of chemisorption-active sites on the surface of oxidized RSi and their reactivity toward methane molecules, we continued the study of this system. We present here the results of an experimental study of the mechanism of methylation of a silica surface containing DOSGs resulting in the formation of surface methoxy and ethoxy groups.

EXPERIMENTAL

Experiments were carried out with samples of highly dispersed Aerosil A-300 in the form of semi-transparent films, 50 – $100 \mu\text{m}$ thick. The methods for the preparation and activation of samples resulting in

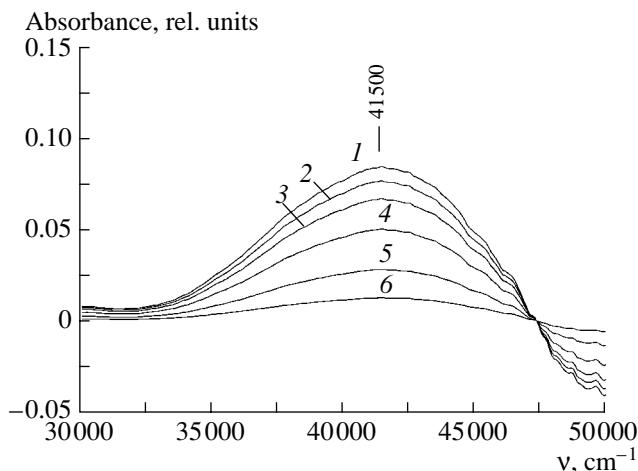


Fig. 1. Changes in the intensity of the optical absorption band of DOSG at 41500 cm^{-1} (5 eV) in a methane atmosphere ($P_{\text{CH}_4} = 0.2$ Torr; 300 K): (1) initial DOSG spectrum, (2) after 5 min, (3) after 40 min, (4) after 2.5 h, (5) after 4.5 h, and (6) after 6 h.

the formation of RSi were analogous to those used earlier in [2, 3, 7].

The main type of diamagnetic defects on the surface of RSi are SSs $(\equiv\text{Si}-\text{O})_2\text{Si}$: [3, 4]. Their concentration is $\sim 10^{13}\text{ cm}^{-2}$ or $\sim 3 \times 10^{19}\text{ g}^{-1}$. To obtain DOSGs, silylene sites were oxidized by molecular oxygen at 295 K [6]:



This method allowed us to quantitatively transform SSs into DOSGs and determine their number in a sample from the amount of oxygen consumed (volumetric method).

These diamagnetic groups can be registered by the optical method [6]. Two relatively low-intense absorption bands with maximums near 41500 and 24200 cm^{-1} (5 and 3 eV) are associated with these groups.

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

The spectra optical absorption of samples were recorded using a Specord-M40 spectrophotometer. IR spectra were recorded using a Digilab Bio-Rad FTS-7 Fourier-transform spectrometer (resolution, $2-4\text{ cm}^{-1}$; number of scans, 256). With this purpose, the sample was placed in a special part of a working cell. ESR spectra of paramagnetic sites were registered using an EPR-20 spectrometer working in an X range. All measurements were carried out at room temperature.

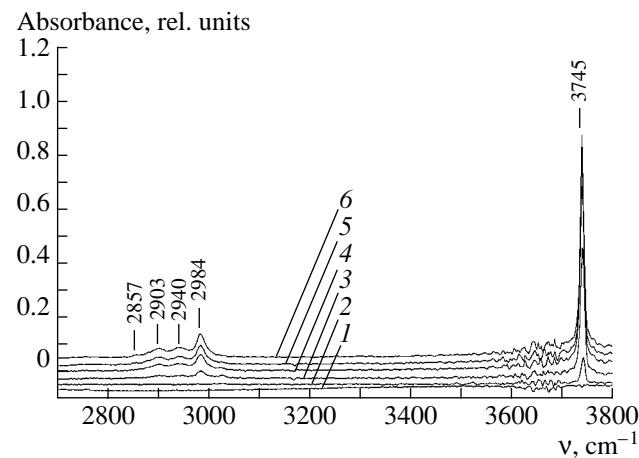


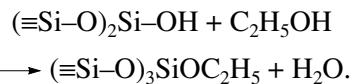
Fig. 2. IR spectra of the products of DOSG interaction with methane ($P_{\text{CH}_4} = 0.2$ Torr; 300 K): (1) initial DOSG spectrum, (2) after 5 min, (3) after 40 min, (4) after 2.5 h, (5) after 4.5 h, and (6) after 6 h.

RESULTS AND DISCUSSION

1. Interaction of Methane with Dioxasilirane Groups

1.1. Reaction of DOSG with methane (the region of low pressures). The sample of oxidized RSi containing $(3.0 \pm 0.1) \times 10^{19}\text{ g}^{-1}$ DOSG was treated with methane at $T = 300\text{ K}$ and $P_{\text{CH}_4} = 0.2$ Torr. Figure 1 shows changes in the intensity of the optical absorption bands of DOSG in the course of the reaction with methane. Simultaneously, we controlled changes in the IR spectra of the sample. The corresponding data are shown in Fig. 2.

In the course of the reaction, we registered the appearance of bands in the region of C–H stretching vibrations at 2857 , 2903 , 2940 , and 2984 cm^{-1} and in the region of O–H stretching vibrations at 3745 cm^{-1} . Several bands in the region of C–H stretching vibrations belong to ethoxy groups. Figure 3 shows the IR spectrum of ethoxy groups for comparison. The latter were obtained by the treatment of a hydrated silica sample with ethanol vapors at 673 K . Under these conditions ethoxy groups substitute for terminal hydroxy groups:



1.2. Reaction of DOSG with methane (the region of high pressures). In another experiment, the reaction of DOSG with methane was carried out at a much higher gas pressure. A sample containing DOSG was kept in contact with methane molecules at a pressure of 250 Torr and 238 K and heated in a gas atmosphere to 300 K . Figure 4 shows the IR spectrum of the sample after heating. Three bands appeared in the spectrum in the region of C–H stretching vibrations at 2859 , 2961 ,

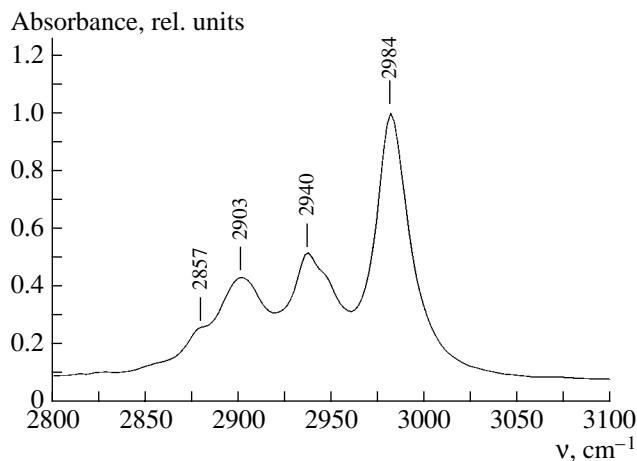


Fig. 3. Fragment of the IR spectrum of the ethoxylated silica surface.

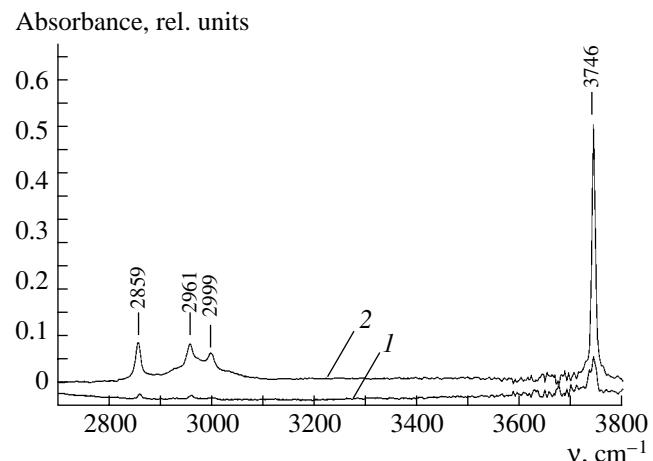


Fig. 4. IR spectrum of the products of DOSG methylation ($P_{\text{CH}_4} = 250$ Torr; 300 K): (1) initial DOSG spectrum and (2) after 5 min upon methane admission.

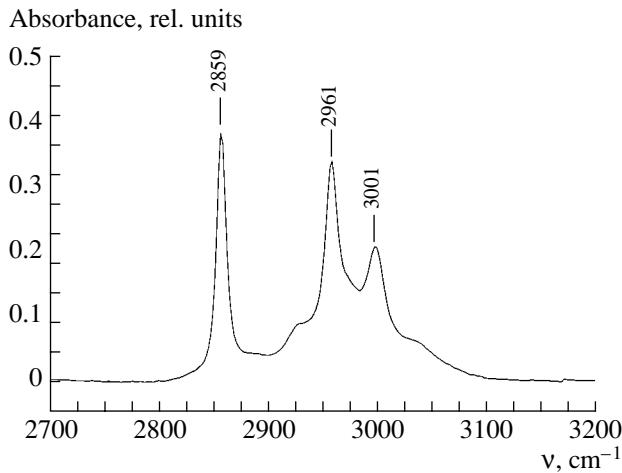
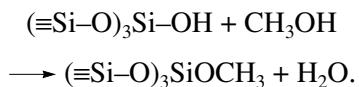


Fig. 5. Fragment of the IR spectrum of the methoxylated silica surface.

and 2999 cm^{-1} and one appeared in the region of O–H stretching vibrations at 3746 cm^{-1} . Figure 5 shows the IR spectrum of the methoxylated silica sample for comparison:



Thus, in this case methylation resulted in the formation of methoxy groups.

1.3. Reaction of DOSG with methane (the region of medium pressures). When the methylation of DOSG was carried out at room temperature and a methane pressure of 50 Torr, the IR spectrum of the reaction products in the region of C–H stretching vibrations was a superposition of signals from methoxy and ethoxy groups (Fig. 6).

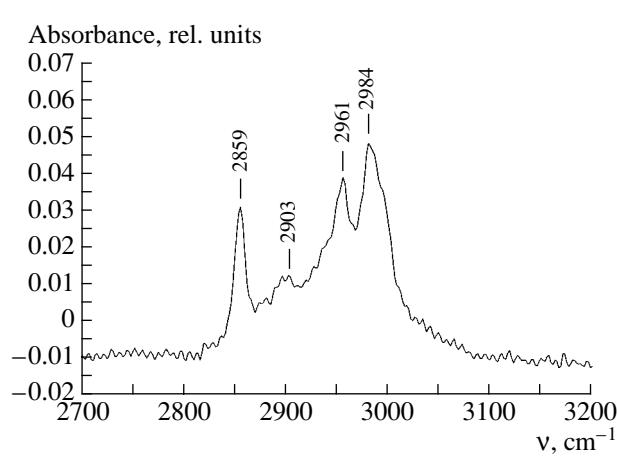
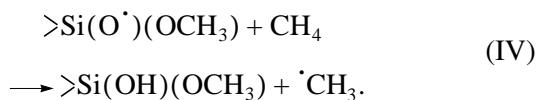


Fig. 6. IR spectrum of the products of DOSG methylation ($P_{\text{CH}_4} = 50$ Torr; 300 K).

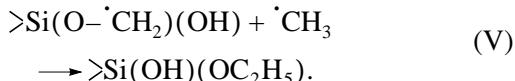
2. Mechanisms of Formation of Ethoxy and Methoxy Groups

Thus, it follows from the experimental data that variations in the methane pressure affect the composition of the products formed in the reaction of DOSG methylation. According to [6], the first step of the process is the interaction of DOSG with a methane molecule is reaction (I) resulting in the formation of a methyl radical and an oxysilyl radical. The methyl radical formed adds to another DOSG (reactions (III) and (IV)). To explain the apparent changes in the composition of products formed, we suppose that the formation of the products of this reaction, a $>\text{Si}(\text{O}^{\cdot}\text{CH}_2)(\text{OH})$ radical, occurs as a result of a stepwise process. The first step produces the $>\text{Si}(\text{O}^{\cdot})(\text{OCH}_3)$ radical (reaction (III)).

In a methane atmosphere, a new channel for the transformation of this radical appears:



This reaction results in the formation of one of the final products (the methoxy group). Another reaction that occurs in this system results in the formation of another final product (the ethoxy group) via the recombination of a methyl radical and a $>\text{Si}(\text{O}^\cdot\text{CH}_2)(\text{OH})$ radical:



The key reactions that control the composition of the final products of the methylation reaction are the reaction of isomerization of oxysilyl radical (IV) and reaction (V). By changing the pressure of methane in the system, one can affect the ratio of the rates of these reactions and the composition of the final products.

According to experimental data, reaction (V) occurs at a high rate at a temperature as low as 77 K; that is, its activation energy is close to zero [8]. Experimental data allow us to estimate the activation energy of reaction (IV). When the DOSG methylation reaction is carried out at 300 K and a methane pressure of 50 Torr, the ratio of the amounts of methoxy and ethoxy groups in the reaction products were comparable ($\sim 1/1$). Assuming that the rate constant of oxy radical interaction with methane (reaction (V)) is $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the time of this reaction can be estimated as 5×10^{-6} s. Therefore, the rate constant of unimolecular hydrogen transfer (reaction (IV)) at 300 K is $2 \times 10^5 \text{ s}^{-1}$. Assuming that the preexponential factor for this unimolecular process is 10^{12} s^{-1} , we obtain the activation energy of this reaction: $\sim 8 \text{ kcal/mol}$.

Our experimental results agree with those reported earlier in [2]. The authors of that work carried out DOSG methylation at room temperature and a methane pressure of ~ 80 Torr. Under these conditions they obtained a mixture of methoxy and ethoxy groups. Thus, by varying the methane pressure, one is able to control the composition of final products.

Note that the reactivity of the carbon-centered radical $>\text{Si}(\text{O}^\cdot\text{CH}_2)(\text{OH})$ toward methane is much lower than that of DOSG [9]. Therefore, under experimental conditions they only participate in the reactions of free radical chain termination (reaction (VI)).

3. Thermal Decomposition of DOSG Methylation Products

(1) The thermal decomposition of the $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{OH})(\text{OC}_2\text{H}_5)$ groups occurs at 723–823 K in agreement with the data reported in [2]. In the course

of pyrolysis, the sample evolves ethylene. The amount of ethylene formed was $(6.8 \pm 0.2) \times 10^{18} \text{ g}^{-1}$ and the amount of DOSG in the sample was $(1.5 \pm 0.2) \times 10^{19} \text{ g}^{-1}$. Since the formation of one ethoxy group is accompanied by the decay of two DOSGs (and the appearance of three hydroxy groups), the results obtained point to the quantitative formation of ethylene in this process.

Heating the sample containing ethoxy groups for 10 min at 873 K led to the complete disappearance of the absorption bands of ethoxy groups and an increase in the intensity of the band of OH group stretching vibrations.

Thus, the thermal decomposition of the $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{OH})(\text{OC}_2\text{H}_5)$ groups occurs according to the following scheme:



After 10 min of heating the sample at 723 K, $\sim 35\%$ of the overall amount of ethylene was evolved. Therefore, we obtain the rate constant of the reaction: k (723 K) $\equiv 9.5 \times 10^{-4} \text{ s}^{-1}$. The activation energy of this process estimated from the above data is 50 kcal/mol (the value of the preexponential factor of this unimolecular process was assumed to be equal to 10^{12} s^{-1}).

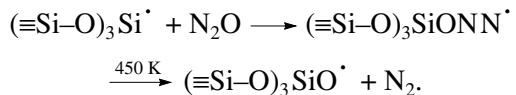
(2) The pyrolysis of methoxy groups begins at temperatures higher than 800 K. The main gaseous products of pyrolysis are hydrogen and CO. We assume that the formation of these products is due to the decomposition of methanol and formaldehyde on the silica surface at high temperatures. Methanol and formaldehyde are the primary products of the decomposition of methoxy groups $>\text{Si}(\text{OH})(\text{OCH}_3)$. The pyrolysis of methoxy groups on the silica surface was studied in [1, 2].

4. Determination of the Ratio of the Rate Constants of Interaction of Methyl Radicals with SSs and DOSGs

One of the reactions involved in the scheme of DOSG methylation is the reaction of methyl radical addition to this group (reaction (III)). Since the expected value of the rate constant is high, its direct measurement is impossible under our conditions. To estimate the value of the rate constant, we used the method of competing reactions. With this goal, we determined the rate constants of methyl radical addition to DOSG and $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot$ (SS). It was shown in [10] that the value of the rate constant of methyl radical addition to SS is $10^{-11 \pm 1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

To solve this problem, we prepared a sample containing oxysilyl radicals $(\equiv\text{Si}-\text{O})_3\text{SiO}^\cdot$, SS, and DOSG. Oxy radicals generated methyl radicals in the reaction with methane molecules, which were accepted

by diamagnetic groups. With this purpose, the RSi sample was used. Then, silyl radicals $(-\text{Si}-\text{O})_3\text{Si}^\cdot$ on the surface of RSi were transformed into the oxy state [3, 4]:



The number of oxy radicals determined from the amount of evolved nitrogen was $(2.8 \pm 0.1) \times 10^{17}$ molecule/g.

Then a portion of SSs was transformed into DOSGs (O_2 chemisorption at room temperature (reaction (I)). The amount of DOSGs (determined by the volumetric method) was $(1.8 \pm 0.1) \times 10^{19}$ g⁻¹. The number of remaining SSs was $(5.4 \pm 0.1) \times 10^{18}$ g⁻¹.

The reaction with methane was carried out at room temperature and a low pressure of methane (3.2×10^{-2} Torr). Under these conditions, the rate of the reaction of methane with DOSG can be neglected (oxy radicals react with methane with an activation energy close to zero). The number of chemisorbed methane molecules was $(3.0 \pm 0.1) \times 10^{17}$ molecule/g, which coincided with the number of oxy radicals within the experimental accuracy.

SSs and DOSGs accept methyl radicals with the formation of the corresponding intermediates [6, 10]:

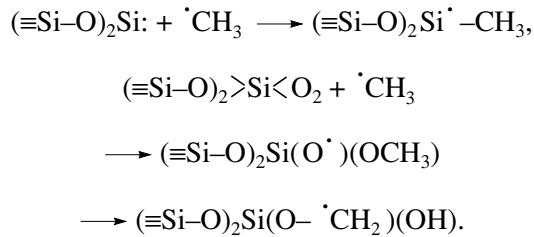


Figure 7a shows the ESR spectrum of the products of this reaction. This is a superposition of the signals from the radicals $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$ (Fig. 7b) and $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{O}-\cdot\text{CH}_2)(\text{OH})$ (Fig. 7c) [6, 11]. The amount of radicals formed was determined from the number of chemisorbed N_2O molecule reacting only with the silyl radical and oxygen, which adds to the carbon-centered radical (the reaction was carried out at an oxygen pressure of 1.5×10^{-3} Torr. Under these conditions, the contribution of other processes with the participation of O_2 can be neglected. The amount of silicon-centered radicals determined by this method was

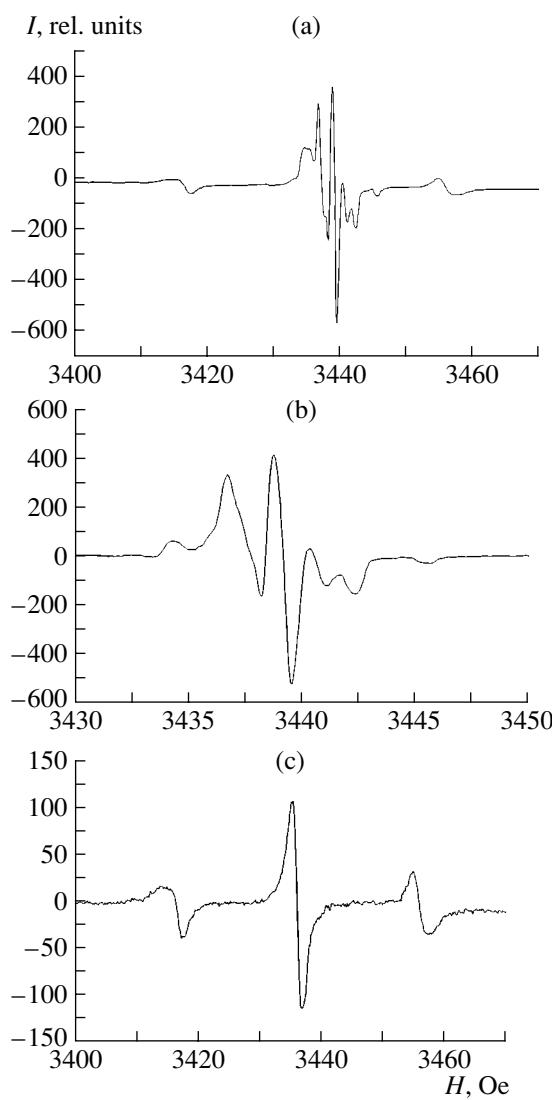


Fig. 7. ESR spectra of paramagnetic sites stabilized on the silica surface (300 K): (a) the products of the reaction of methyl radicals with SS and DOSG, (b) radicals $(\equiv\text{Si}-\text{O})_2\text{Si}^\cdot-\text{CH}_3$, and (c) radicals $(\equiv\text{Si}-\text{O})_2\text{Si}(\text{O}-\cdot\text{CH}_2)(\text{OH})$.

1.82×10^{17} , and the number of carbon-centered radicals was 1.3×10^{17} g⁻¹.

Based on the above data, we estimated the ratio of the rate constants of methyl radical interaction with SS (k_1) and DOSG (k_2):

$$k_1/k_2 = [(N(\text{DOSGs})N(>\text{Si}^\cdot-\text{CH}_3))]/[N(\text{SSs})N(>\text{Si}(\text{O}-\cdot\text{CH}_2)(\text{OH}))] = 4.6 \pm 1.$$

Thus, SSs accept methyl radicals more efficiently than DOSG. However, both of these processes are characterized by the low activation barriers and their rate constants are close to the gas-kinetic constants.

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