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Intramolecular Rearrangements of $>Si(O–C^{\bullet}=O)(CH_2–CH_3)$ and $>Si(CH_2–CH^{\bullet}–CH_3)(CH_2–CH_3)$ Radicals

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Abstract—Using ESR and IR spectroscopy, the structures of $>Si(O–C^{\bullet}=O)(CH_2–CH_3)$ (1) and $>Si(CH_2–CH^{\bullet}–CH_3)(CH_2–CH_3)$ (2) radicals were deciphered. The directions and kinetic parameters of reactions of intramolecular rearrangements in these radicals were determined. The reactions of hydrogen atom abstraction in radical (1) from the CH_2 and CH_3 groups were studied. It was found that the endothermic reaction of hydrogen atom abstraction from the methyl group occurs at a higher rate than the exothermic reaction with the methylene group. The differences are determined by changes in the size of a cyclic transition state. Based on the experimental data, the strengths of separate C–H bonds in surface fragments are compared. The rearrangement $>Si(CH_2–CH^{\bullet}–CH_3)(CH_2–CH_3) \longrightarrow >Si(C^{\bullet}(CH_3)_2)(CH_2–CH_3)$ was discovered and its mechanism was determined. One of its steps is the skeletal isomerization $\equiv Si_{\gamma}–C_{\beta}(2)–C^{\bullet}_{\alpha}(1) \longrightarrow Si_{\gamma}–C_{\beta}(1)–C^{\bullet}_{\alpha}(2)$. Experimental data are analyzed using the results of quantum-chemical calculations of model systems.

INTRODUCTION

A new method has been proposed for obtaining free-radical intermediates grafted on the surface of reactive silica [1–3]. The availability of the surface defects of a solid for ambient molecules enables purposeful chemical modification and obtaining intermediates with various structures. Specifically, the method has been developed for obtaining the surface structures of the $(\equiv Si–O)_2Si(R_1)(R)$ type (henceforth, a fragment of a solid that involves a two-coordinated silicon atom $(\equiv Si–O–)_2Si$ will be denoted as $>Si$). Fragments R and R_1 may be of different chemical natures; specifically, one of them may be paramagnetic. Thus, two different chemical groups R and R_1 can be made spatially close. This extends the range of intermediates constructed on solid surfaces and enables the study of new chemical processes with their participation, including reactions between groups R and R_1. Earlier, this method was applied to the study of H(D) atom transfer from one hydrocarbon fragment to another [3]: R (CH_3, C_2H_5) and R_1 ($CH_2–CH^{\bullet}_2$, $CD_2–CD^{\bullet}_2$). In this study, we continue along this line. This paper deals with the reactions of intramolecular rearrangements of the radicals $>Si(O–C^{\bullet}=O)(CH_2–CH_3)$ and $>Si(CH_2–HC^{\bullet}–CH_3)$ $(CH_2–CH_3)$.

EXPERIMENTAL

An Aerosil A-300 sample ($m \approx 0.2$ g) with an initial specific surface area of ~300 m^2/g was loaded in a quartz ampule for ESR measurements. The latter was connected to a vacuum system and the sample was calcined in an oxygen atmosphere at 1200 K to remove various chemisorbed species from the surface. Then, the sample surface was methoxylated at 680 K, allowed to stay in a medium of dry methanol vapor (50–100 torr) for 15 min. The methoxylation procedure was repeated two times with the removal of unreacted methanol residues by evacuation at 680 K. Then, the sample was heated to 1250 K along with uninterrupted evacuation of pyrolysis products formed and allowed to stay at this temperature for 20 min. After this treatment the so-called reactive silica sample was obtained, which exhibited high chemisorption activity [4, 5].

The procedure for obtaining the $>Si(\dot{R}_1)(R)$ structure is based on the chemical modification of diamagnetic centers on the silica surface. These centers contain a two-coordinated silicon atom (silylene-type centers $>Si:$). They are stabilized on the reactive silica surface [4, 5] and efficiently accept low-molecular radicals ($R^{\bullet} = H^{\bullet}, D^{\bullet}, C^{\bullet}H_3, O^{\bullet}H, N^{\bullet}H_2$, and others [2]) to form the corresponding paramagnetic complexes:

$$>Si: + R^{\bullet} \longrightarrow >Si^{\bullet}R. \qquad (I)$$

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To generate the $R^{\bullet}$ radicals, the oxy radicals $(\equiv Si{-}O)_3Si{-}O^{\bullet}$ [6],

$$(\equiv Si{-}O)_3Si{-}O^{\bullet} + R{-}H(D)$$

$$\longrightarrow (\equiv Si{-}O)_3Si{-}O{-}H(D) + R^{\bullet}$$

or diamagnetic groups $>Si<O_2$ [7],

$$>Si<O_2 + R{-}H(D) \longrightarrow\ >Si(O^{\bullet})(O{-}H(D)) + R^{\bullet},$$

$$>Si(O^{\bullet})(O{-}H(D)) + R{-}H(D)$$

$$\longrightarrow\ >Si(O{-}H(D))(O{-}H(D)) + R^{\bullet}$$

were used. The procedure for their preparation on the reactive silica surface was described in [3, 8]. By selecting the R–H(D) molecule, it is possible to obtain desired radicals $R^{\bullet}$. The ${}^{\bullet}C_2H_5$ radicals were obtained from ethane molecules.

By dragging silyl-type radicals formed by reaction (I) into a reaction with other molecules containing multiple chemical bonds (C_2H_4, C_2H_2, CO_2, N_2O, etc.), it is possible to obtain new paramagnetic complexes. To obtain radicals that are studied in this work, we used carbon dioxide and propylene molecules:

$$>Si^{\bullet}(CH_2{-}CH_3) + CO_2 \longrightarrow\ >Si(O{-}C^{\bullet}{=}O)(CH_2{-}CH_3), \quad \text{(II)}$$

$$>Si^{\bullet}(CH_2{-}CH_3) + CH_2{=}CH(CH_3) \longrightarrow\ >Si(CH_2{-}HC^{\bullet}{-}CH_3)(CH_2{-}CH_3). \quad \text{(III)}$$

Both reactions were carried out at room temperature at $P_{CO_2} \approx 1$ torr or $P_{C_3H_6} \approx 10^{-2}$ torr. The extent of reaction was controlled by ESR.

ESR spectra of radicals were recorded using an EPR-20 radiospectrometer working in an X-range (a frequency of 9.1 MHz). The frequency of high-frequency modulation was 100 kHz. The magnetizing force was registered using an NMR magnetometer. The radiospectrometer was connected to a PC through an interface. At 77 K, ESR spectra were registered by putting the sample into a quartz Dewar bottle filled with liquid nitrogen. The constant temperature of the sample in the resonator was maintained by a flow of gaseous nitrogen.

IR spectroscopic measurements were carried out for the samples that were made of pressed 50–100-μm thick highly-dispersed semitransparent films of Aerosil [8]. For these samples, one can register the IR spectra at wavenumbers in the region of ≥1300 cm^{-1} in the window of quartz glass transparency (850–950 cm^{-1}). The films were placed into a special cell with silica windows. IR spectra were recorded at room temperature using a Digilab Fourier-transform spectrometer with 4 cm^{-1} resolution and 256–1024 scans.

The structures of molecules, radicals, and transition states for different channels of their transformation were optimized by minimizing the gradient norm using Gaussian-94 [9] or using the DFT method [10, 11]. For all optimized structures, vibrational spectra were simulated. Each transition state had one negative eigenvalue of the Hessian matrix.

RESULTS AND DISCUSSION

After carrying out reaction (II) and obtaining radicals $>Si(O{-}C^{\bullet}{=}O)(CH_2{-}CH_3)$, a low-intensity signal of some paramagnetic center was registered in the sample at room temperature together with the ESR spectrum of oxycarbonyl radicals [7, 12]. It had a distinctive hyperfine structure: a triplet with splitting constants of 21.7 and 20.4 G (signal registration temperature, 300 K). This belonged to the $>Si(O{-}CH{=}O)(C_{\beta}H_2{-}C_{\alpha}H_2^{\bullet})$ radical (the hyperfine interaction constants refer to protons bound to the C_{α} and C_{β} atoms, respectively). A similar ESR spectrum has been registered earlier for the $\equiv Si{-}CH_2{-}CH_2^{\bullet}$ radical [1]. Thus, in this system, the hydrogen transfer process occurs even at 300 K:

$$>Si(O{-}C^{\bullet}{=}O)(CH_2{-}CH_3)$$

$$\longrightarrow\ >Si(O{-}CH{=}O)(CH_2{-}CH_2^{\bullet}).$$

Figure 1 shows the kinetics of changes in the concentrations of radicals at the stage of their preparation (reaction (II)). The synchronous increase in the concentrations of radicals $>Si(O{-}C^{\bullet}{=}O)(CH_2{-}CH_3)$ and $>Si(O{-}CH{=}O)(CH_2{-}CH_2^{\bullet})$ in the course of this reaction points to the fact that equilibrium is established between these two radicals at room temperature:

$$>Si(O{-}C^{\bullet}{=}O)(CH_2{-}CH_3)$$

$$\xrightleftharpoons{K_p(1)}\ >Si(O{-}CH{=}O)(CH_2{-}CH_2^{\bullet}).$$

The time of establishment of this equilibrium is much shorter than the characteristic time of CO_2 molecule addition to the $>Si^{\bullet}(C_2H_5)$ radical. At 0.1 torr, the characteristic time of the reaction at 295 K is several minutes. The rate constant of this process is $K_p(1)(295\ K) = 0.08 \pm 0.02$.

If the sample is allowed to stay at room temperature for a long time (several hours), new radicals are formed in the system:

$$>Si(O{-}C^{\bullet}{=}O)(CH_2{-}CH_3)$$

$$\xrightleftharpoons{K_p(2)}\ >Si(O{-}CH{=}O)(CH^{\bullet}{-}CH_3).$$

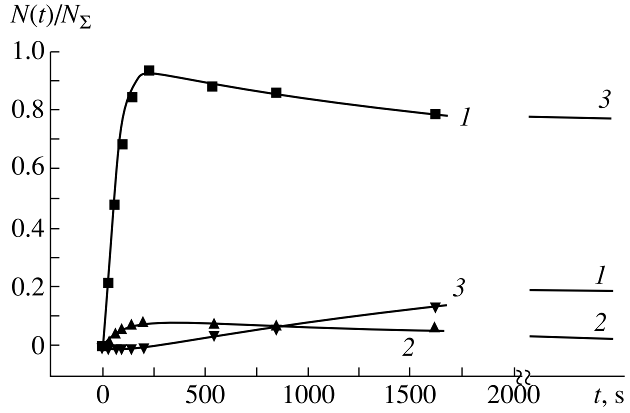


Fig. 1. Kinetics of free radical accumulation in the >Si$^\bullet$(CH$_2$–CH$_3$) + CO$_2$ system (N_Σ = const is the overall amount of radicals in the system, T = 295 K): (*1*) >Si(O–C$^\bullet$=O)(CH$_2$–CH$_3$), (*2*) >Si(O–CH=O)(CH$_2$–CH$_2^\bullet$), and (*3*) >Si(O–CH=O)(CH$^\bullet$–CH$_3$). The equilibrium concentrations of radicals in this system are shown in the right-hand side.

The ESR spectrum of the last radical has a distinctive form stipulated by the anisotropic hyperfine interaction of an unpaired electron with the α-H atom ($a_\parallel(\mathrm{H}_\alpha)$ = 28 G, $a_\perp(\mathrm{H}_\alpha)$ = 18.5 G) and three protons of the methylene group ($a(\mathrm{H}_\beta)$ = 25.4 G). A similar ESR spectrum was registered for the >Si(CH$_2$–CH$_3$)(CH$^\bullet$–CH$_3$) radical [3]. In this radical, shifts of the α-proton are possible due to internal rotation around the Si–C bond. This rotation can only lead to the partial averaging of the anisotropy of hyperfine interaction.

The kinetics of this process was monitored using the ESR method by tracing the intensities of the ESR spectrum of the >Si(O–C$^\bullet$=O)(CH$_2$–CH$_3$) radical and an increase in the intensities of signals from the >Si(O–CH=O)(CH$^\bullet$–CH$_3$) radical.

A general picture of changes in the concentrations of radical of various types in this system at room temperature is shown in Fig. 1. After long standing, equilibrium is established between the three types of free radicals participating in the process. The equilibrium constant based on these data $K_p(2)$ at 293 K was 4.0 ± 0.5.

Knowing the equilibrium constants $K_p(1)$ and $K_p(2)$, we estimate the equilibrium constant of the reaction

$$>\mathrm{Si(O{-}CH{=}O)(CH^\bullet{-}CH_3)}$$

$$\xrightleftharpoons{K_p(3)} >\mathrm{Si(O{-}CH{=}O)(CH_2{-}CH_2^\bullet)}.$$

At 295 K, it is $K_p(3) \approx 0.02$. As expected, the >Si(O–CH=O)(CH$^\bullet$–CH$_3$) radical is more stable than the >Si(O–CH=O)(CH$_2$–CH$_2^\bullet$) radical. For a similar process >Si(CH$_2$–CH$_3$)(CH$_2$–CH$_2^\bullet$) $\rightleftharpoons$ >Si(CH$_2$–CH$_3$)(CH$^\bullet$–CH$_3$), it only became possible to estimate the upper limit of the corresponding equilibrium constant [3]: ≤0.1.

Figure 2 shows the kinetic curve of the formation of radicals >Si(O–CH=O)(CH$^\bullet$–CH$_3$) in the reaction >Si(O–C$^\bullet$=O)(CH$_2$–CH$_3$) $\longrightarrow$ >Si(O–CH=O)(CH$^\bullet$–CH$_3$). This process follows the first order up to high reaction extents, and its rate constant k(295 K) is $(7.0 \pm 0.7) \times 10^{-5}$ s^{-1}.

RESULTS OF IR SPECTROSCOPIC MEASUREMENTS

Information on the products of free-radical transformations obtained by ESR and presented in the preceding section was supplemented by the results of IR spectroscopic data. The formation of the >Si$^\bullet$(CH$_2$–CH$_3$) radicals in the course of reaction (I) is accompanied by the appearance of several bands in the IR spectrum of the sample in the region of C–H bond stretching vibrations (Fig. 3a, spectrum *1*). An analogous spectrum was obtained in [13]. More intense bands at 2975 and 2893 cm^{-1} were assigned to the antisymmetrical vibrations of the methyl group. Less intense bands were observed between these two. They can be assigned to the vibrations of C–H bonds in the methyl group (Table 1). The addition of CO$_2$ molecules to these radicals results in a small shift (several cm^{-1}) toward higher wavenumbers (Fig. 3, spectrum *2*). Analogous effects were observed in the addition of a oxygen molecule to >Si$^\bullet$(CH$_2$–CH$_3$) resulting in the formation of the peroxy radical >Si(–O–O$^\bullet$)(CH$_2$–CH$_3$) [13].

The formation of the oxyacyl radical resulted in the appearance of the new intense band with a maximum of absorbance at 1825 cm^{-1} (Fig. 3, spectrum *4*). This band is due to the stretching vibration of the C=O–O–C$^\bullet$=O group (see below). After allowing the sample to stay at room temperature for several hours, equilibrium is established between different forms of radicals. In the course of this process, the main portion (~80%, see Fig. 1) of radicals >Si(–O–C$^\bullet$=O)(CH$_2$–CH$_3$) transforms into >Si(O–CH=O)(CH$^\bullet$–CH$_3$). In the IR spectra, this transformation reveals itself as follows. The intensity of the band of the C=O stretching vibration at 1825 cm^{-1} decreases. A band at 1742 cm^{-1} synchronously appears and becomes more intense (Fig. 3, spectrum *5*). Restructuring of the IR spectrum in the region of C–H bond stretching vibrations occurs in parallel (Fig. 3, spectrum *3*): the bands at 2983 and 2897 cm^{-1} become less intense and new bands appear, of which the band at 2947 cm^{-1} is the most intense. We did not manage to isolate the absorption bands of the >Si(O–CH=O)(CH$_2$–CH$_2^\bullet$) radicals in the sample (their concentration is below 10% of the overall amount of centers participating in transformations).

Table 1 shows the results of calculations of frequencies and intensities of the stretching vibrations of the C–H and C=O bonds in radicals $F_2Si^{\bullet}(CH_2–CH_3)$ (**1**), $F_2Si(O–C^{\bullet}=O)(CH_2–CH_3)$ (**2**), $F_2Si(O–CH=O)(CH_2–CH_2^{\bullet})$ (**3**), and $F_2Si(O–CH=O)(CH^{\bullet}–CH_3)$ (**4**), which are the models of surface centers.

The calculated vibration frequencies differ from the experimental ones because the calculation gives the values of harmonic frequencies and because there is some inaccuracy in the determination of the molecule force field. For empirical correction ($\nu(1)_{corr}$) of the calculated value ($\nu(1)_{calcd}$) value of the frequency of normal vibration, we used the following procedure. The frequency of a similar vibration was calculated at the same theoretical level in the molecule with a similar chemical structure ($\nu(2)_{calcd}$) for which the experimental data ($\nu(2)_{exp}$) is available and then the calculated value was corrected:

$$\nu(1)_{corr} = \nu(1)_{calcd}\nu(2)_{exp}/\nu(2)_{calcd}.$$

This value was compared with the experimental values.

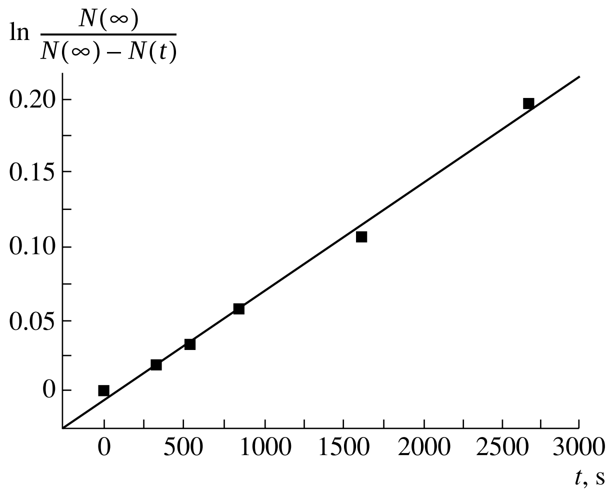


Fig. 2. Kinetics of radical $>Si(O–CH=O)(CH^{\bullet}–CH_3)$ formation in the course of the process $>Si(O–C^{\bullet}=O)(CH_2–CH_3) \longrightarrow >Si(O–CH=O)(CH^{\bullet}–CH_3)$ ($T = 295$ K) describe in the semilogarithmic coordinates ($N(t)$ is time-dependent radical concentration).

In the calculation of the vibration frequencies of C=O and C–H bonds in the $\equiv Si–O–C^{\bullet}=O$ and $\equiv Si–O–CH=O$ groups $F–C^{\bullet}=O$ and $F–CH=O$ were used as test molecules [14] (the F atom and the $\equiv Si–O–$ group have similar properties as substituents [8]). For the radical, $\nu(C=O)_{exp} = 1855$ [14] and $\nu(C=O)_{calcd}$ =

Table 1. Results of quantum-chemical calculations of the vibration frequencies in the radicals $F_2Si^{\bullet}(C(1)H_2–C(2)H_3)$ (1), $F_2Si(O–C^{\bullet}=O)(CH_2–CH_3)$ (2), $F_2Si(O–CH=O)(CH_2–CH_2^{\bullet})$ (3), and $F_2Si(O–CH=O)(CH^{\bullet}–CH_3)$ (4) (DFT calculation in the *tz*-basis [11]); ν_{corr} are the corrected values of frequencies (see text)

Assignment	Vibration frequency, cm^{-1} (intensity, KM/mol)			
	1	**2**	**3**	**4**
$\nu(C=O)$	–	1824(354)	1742(306)	1744(311)
$\nu(C–H)$*	–	–	2955(51)	2955(61)
$\nu(C(1)–H)$	2975(6)	2971(1.6)	2956(16)	3087(5)
	3019(1)	3012(0.4)	3014(2)	–
$\nu(C(2)–H)$	2967(25)	2977(30)	3097(8)	2916(9)
	3033(14)	3045(14)	3202(3.5)	2964(10)
	3054(17)	3051(16)	–	3044(7)
$\nu_{corr}(C=O)$	–	1828 {1825}**	1750	1752 {1742}
$\nu_{corr}(C–H)$*	–	–	2937	2937 {2947}
$\nu_{corr}(C(1)–H)$	2898	2894		3026
	2965	2958		
$\nu_{corr}(C(2)–H)$	2902 {2892}	2912 {2897}	3045	2798
	2981 {2977}	2993 {2983}	2130	2844
	3000	2997		2921

* In the CH=O group.

** Experimental values of frequencies are given in parentheses.

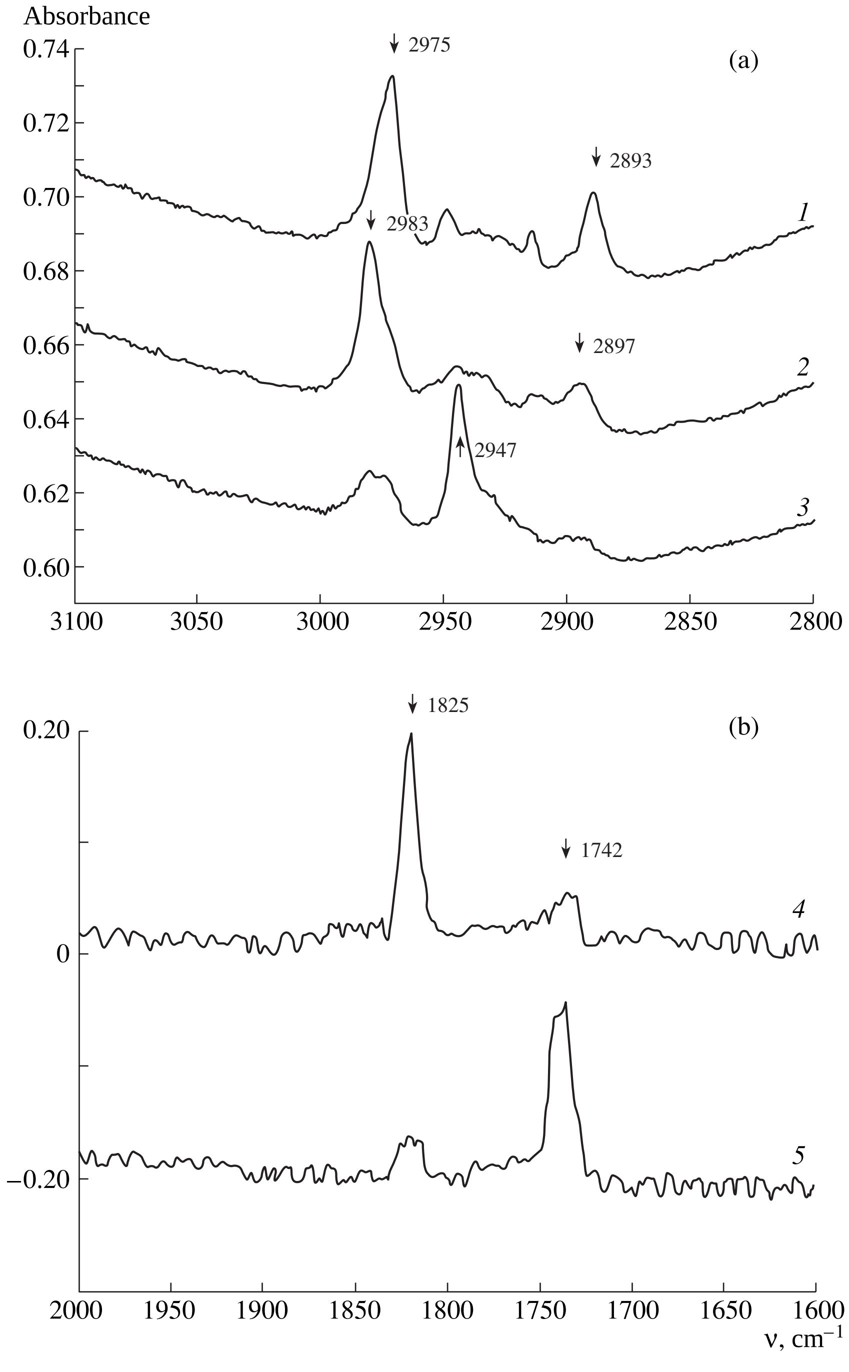


Fig. 3. IR spectra of radicals formed in the $>\mathrm{Si}^{\bullet}$ $(CH_2–CH_3)$ + CO_2 system: (*1*) $>\mathrm{Si}^{\bullet}$ $(CH_2–CH_3)$; (*2*, *4*) after the treatment of sample 1 by CO_2 molecules at 300 K; (*3*, *5*) after allowing sample 2 to stay for 10 h at 300 K.

1851 cm^{-1}. For the molecule, $\nu(C{=}O)_{exp}$ = 1837 [14], $\nu(C{=}O)_{calcd}$ = 1829 cm^{-1}, $\nu(C–H)_{exp}$ = 2981 [14], and $\nu(C–H)_{calcd}$ = 2999 cm^{-1}. Thus, the scaling factors for these frequencies were close to unity.

In estimating the frequencies of C–H vibrations in hydrocarbon fragments, we compared experimental data and the results of calculation for the $CH_3–CH_2–CH_3$ molecule and the $CH_3–\dot{C}H_2$ radical. For the methylene group in the C_3H_8 molecule, $\nu(C–H)_{exp}$ = 2875 and 2922 cm^{-1} [15] and $\nu(C–H)_{calcd}$ = 2951 and 2975 cm^{-1}. For the methyl group, $\nu(C–H)_{exp}$ = 2890, 2969, and 2973 cm^{-1} [15], and $\nu(C–H)_{calcd}$ = 2955, 3021, and 3024 cm^{-1}. For the radical, $\nu(C–H)_{exp}$ = 2840 [16] and $\nu(C–H)_{calcd}$ = 2960 cm^{-1}; in the methyl group,

$\nu(\text{C–H})_{\text{exp}}$ = 3032.5 and 3112.5 [16] and $\nu(\text{C–H})_{\text{calcd}}$ = 3084 and 3184 cm^{-1} for the methylene group.

The bottom part of Table 1 shows the results of corrected calculations and the values of experimental frequencies (in parentheses). As follows from these data, the bands in IR spectra at 1825, 1742, and 2947 cm^{-1} are stipulated by the stretching vibration of the C=O and C–H bonds in the $\equiv$Si–O–$\text{C}^{\bullet}$=O and $\equiv$Si–O–CH=O fragments. The assignment of the bands of C–H bond stretching vibrations in the hydrocarbon fragments of the $>\text{Si}^{\bullet}(\text{CH}_2\text{–CH}_3)$ and $>\text{Si}(\text{O–C}^{\bullet}\text{=O})(\text{CH}_2\text{–CH}_3)$ radicals is generally acceptable. The calculations correctly predict an increase in the frequencies of these vibrations when passing from the first radical to second.

Thus, using IR spectroscopy, we obtained data on the structure and spectral characteristics of the products of free radical rearrangements in the $>\text{Si}(\text{O–C}^{\bullet}\text{=O})(\text{CH}_2\text{–CH}_3)$ radical and confirmed that they are stipulated by the intramolecular reactions of hydrogen atom transfer.

Estimates of C–H Bond Strengths

Data obtained on the equilibrium constants of reactions $>\text{Si}(\text{R}^{\bullet})(\text{CH}_2\text{–CH}_3) \rightleftharpoons >\text{Si}(\text{R–H})(\text{CH}_2\text{–C}\dot{\text{H}}_2)$, where $\text{R}^{\bullet} = \text{CH}_2\text{–C}\dot{\text{H}}_2$, $\text{C}\dot{\text{H}}_2$, $\text{CH}^{\bullet}\text{–CH}_3$, and $\text{O–C}^{\bullet}\text{=O}$ (see also [3]) can be used in estimating the C–H bond strengths in the systems under study.

Table 2 presents data on the ratio of the concentrations (relative to $>\text{Si}(\text{CH}_2\text{–C}\dot{\text{H}}_2)(\text{R})$) of different radicals in the sample (T = 295 K; under equilibrium conditions).

The equilibrium constant is determined by the expression $K_{\text{p}} = \exp(\Delta S/R)\exp(-\Delta H/RT)$, where ΔS is the entropy change of reaction products and the initial system; ΔH is the difference in the enthalpies of their formation, which is largely determined by the differences in the corresponding C–H bond strengths. Assuming that $\Delta S \approx 0$, these differences can be determined from the obtained experimental data (see Table 2). The absolute values of bond energies were obtained assuming that the strength of the C–H bond in the methyl group of the $>\text{Si}(\text{R})(\text{CH}_2\text{–CH}_3)$ fragments is 100.4 kcal/mol, as well as in the CH_3 group in the ethane molecule [17] and does not depend on R.

The obtained results are shown in Table 3. They allow us to compare the effects of substituents involving the C and Si atoms on the strength of the C–H bond.

In the series CH_4, $\text{CH}_3\text{–CH}_3$, $\text{CH}_3\text{–CH}_2\text{–CH}_3$, the strengths of C–H bonds are 105, 100.4, and 97 kcal/mol, respectively [17]. According to the experimental data, the strength of the C–H bond in the methylene group of the $>\text{Si}(\text{CH}_2\text{–CH}_3)(\text{R})$ fragment is 2 kcal/mol lower than the C–H bond strength in the CH_3 group. Consequently, the replacement of the CH_3 substituent by the $(\equiv\text{Si–O})_2(\text{R})\text{Si–}$ group results in an increase in the strength of the C–H bond by ≈1.5 kcal/mol.

Table 2. The ratio of radical concentrations of different types* (T = 295 K, equilibrium)

Radical structure	Ratio of concentrations
$>\text{Si}(\text{CH}_2\text{–C}\dot{\text{H}}_2)(\text{C}_2\text{H}_5)$	1
$>\text{Si}(\text{CH}^{\bullet}\text{–CH}_3)(\text{C}_2\text{H}_5)$	48
$>\text{Si}(\text{C}\dot{\text{H}}_2)(\text{C}_2\text{H}_5)$	<0.1
$>\text{Si}(\text{O–C}^{\bullet}\text{=O})(\text{C}_2\text{H}_5)$	12

* Relative to the $>\text{Si}(\text{CH}_2\text{–C}\dot{\text{H}}_2)(\text{R})$, where R = CH_3, C_2H_5, O–CH–O radical.

This conclusion is supported by data from [3] obtained for the reaction

$$>\text{Si}(\text{CH}_2\text{–C}\dot{\text{H}}_2)(\text{CH}_3) \longleftrightarrow >\text{Si}(\text{CH}_2\text{–CH}_3)(\text{C}\dot{\text{H}}_2).$$

The equilibrium in this process is shifted to the left at room temperature and we only have an estimate of the equilibrium constant for this process, $K_{\text{p}} < 0.1$. Assuming that ΔH = 1.5 kcal/mol for this process (see above), we obtain $K_{\text{p}} = \exp(-1500/600) = 0.08$.

The strength of the C–H bond in the $\equiv$Si–O–CH=O fragment is somewhat lower than in the methyl group of ethane molecule. Note that, according to the earlier kinetic data [18], the activation energy of hydrogen atom abstraction from the hydrogen molecule by the $\equiv\text{Si–O–C}^{\bullet}\text{=O}$ radical (12 kcal/mol) is higher than the respective activation energy in the case of abstraction by the $\equiv\text{Si–O–CH}_2\text{–C}\dot{\text{H}}_2$ radical (10.5 kcal/mol).

Skeletal Isomerization of Organosilicon Radicals

The reactivity of hydrocarbon radicals in the reactions of hydrogen atom transfer depends on the nature of substituents at a carbon atom. Experimental data have been obtained for the $>\text{Si}(\text{CH}_2\text{–C}\dot{\text{H}}_2)(\text{R})$ radicals with R = CH_3 and C_2H_5 [3]. In this section, we present the results of the experimental study of the $>\text{Si}(\text{CH}_2\text{–CH}^{\bullet}\text{–CH}_3)(\text{CH}_2\text{–CH}_3)$ radical.

The reactivity of secondary hydrocarbon radicals is lower than the reactivity of primary radicals, and we could expect that such a substitution would result in a

Table 3. The strength of the C–H bond (*E*) in the studied structures

Structure	*E*, kcal/mol
$>\mathrm{Si(CH_2{-}CH_2{-}H)(R)}$	100.4
$>\mathrm{Si(}\underset{\mathrm{H}}{\underset{\vert}{\mathrm{C}}}\mathrm{H{-}CH_3)(R)}$	98.5
$>\mathrm{Si(CH_2{-}H)(R)}$	≥102
$>\mathrm{Si(O{-}}\underset{\mathrm{H}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}O)(R)}$	99.5

change in the equilibrium constant and a decrease in the rate of establishing the corresponding equilibrium.

Figure 4a shows the ESR spectrum of the radical that is formed by the addition of a propylene molecule to the silyl radical $>\mathrm{Si}^{\bullet}(\mathrm{C_2H_5})$ at room temperature:

$$>\mathrm{Si}^{\bullet}(\mathrm{CH_2{-}CH_3}) + \mathrm{CH_2{=}CH(CH_3)}$$

$$\longrightarrow\ >\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}.$$

The hyperfine structure of the ESR spectrum is due to the interaction of an unpaired electron with one α-proton and two β-protons of the methylene group and three β-protons of the methyl group, respectively. The corresponding hyperfine interaction constants are 20.4, 17.8, and 23.2 G. Close radiospectroscopic characteristics were obtained earlier for the $\equiv\mathrm{Si{-}CH_2{-}CH^{\bullet}{-}CH_3}$ radical [1].

The magnetic equivalence of methyl-group protons and the proximity of the corresponding hyperfine interaction constant to the case of its free rotation suggest that the frequency of methyl group rotation in the radical at 295 K is higher than 10^9 s^{-1} [19]. The observed values of the constants of hyperfine interaction with the protons of a methylene group suggest that the silicon atom in the equilibrium conformation holds the position corresponding to the converging of the $\mathrm{C_\beta}$–Si bond and the axis of the unpaired electron orbital [1].

It was expectable that hydrogen atom abstraction from an adjacent $\mathrm{CH_2}$ group (1,4-transfer) is possible for the $>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$ and $>\mathrm{Si(CH_2{-}CH_2^{\bullet})(CH_2{-}CH_3)}$ radicals [3]:

$$>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$$

$$\longrightarrow\ >\mathrm{Si(CH_2{-}CH_2{-}CH_3)(CH^{\bullet}{-}CH_3)}.$$

For the $>\mathrm{Si(CH_2{-}CH_2^{\bullet})(CH_2{-}CH_3)}$ radical, the rate constant of 1,4-transfer at room temperature is $k(295\ \mathrm{K}) = (1.2 \pm 0.1) \times 10^{-4}\ \mathrm{s^{-1}}$ [3]. For the reaction with the participation of the $>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$ radical, this constant should be lower because of the lower reactivity of the isopropyl radical.

If the sample is allowed to stay at 295 K for 30 min, its ESR spectrum does not change noticeably. To speed the process up, the temperature was increased to 373 K. If the sample is allowed to stay at this temperature, the intensity of the ESR signal from the $>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$ radical decreases by several times and new paramagnetic signals appear (see Fig. 4b). The ESR spectrum of the radical formed in the course of this reaction consists of seven equidistant, isotropic, well-resolved lines with a hyperfine interaction constant of 23 G. The ratio of intensities was close to binomial and the g-factor was 2.0027 ± 0.0003. The observed hyperfine structure of the ESR spectrum is due to six magnetically equivalent β-protons of two methyl groups. At the marginal components of the spectrum, satellite lines were registered at high amplification (these are marked with stars in Fig. 5). These lines are due to the interaction of an unpaired electron with the nucleus of silicon isotope ^{29}Si (the natural concentration of the isotope is 4.7%, $I = 1/2$). The value of the splitting constant $a_{\mathrm{iso}}(^{29}\mathrm{Si}) = (16.0 \pm 1.5)$ G is typical of the silicon atom, which is a substituent at the α-carbon atom of the radical [20].

Based on the radiospectroscopic characteristics discussed above, this ESR spectrum should be assigned to the $>\mathrm{Si(C^{\bullet}(CH_3)_2)(CH_2{-}CH_3)}$ radical. The fact that the formed radical contains $\mathrm{C_2H_5}$ as a second substituent at the silicon atom was proven as described below. It is known [20] that peroxy hydrocarbon radicals containing a silicon atom as an α-substituent decomposes even at <270 K by the reaction:

$$\equiv\mathrm{Si{-}CH(R)(O{-}O^{\bullet})} \longrightarrow\ \equiv\mathrm{Si{-}O^{\bullet}} + \mathrm{H(R)C{=}O}.$$

As a result of this reaction, the oxysilyl radical is formed, which is highly reactive in the reactions of hydrogen abstraction [6]. When the silicon atom has hydrocarbon substituent R, the oxy radical abstracts a hydrogen atom from this group. Information on the structure of R can be obtained by deciphering the structure of the radical formed.

A peroxy radical was obtained by the oxidation of the hydrocarbon by molecular oxygen at 173 K:

$$>\mathrm{Si(C^{\bullet}(CH_3)_2)(CH_2{-}CH_3)} + \mathrm{O_2}$$

$$\longrightarrow\ >\mathrm{Si(C(O{-}O^{\bullet})(CH_3)_2)(CH_2{-}CH_3)}.$$

At this temperature, the peroxy radical is stable. When the system is heated to room temperature, peroxy

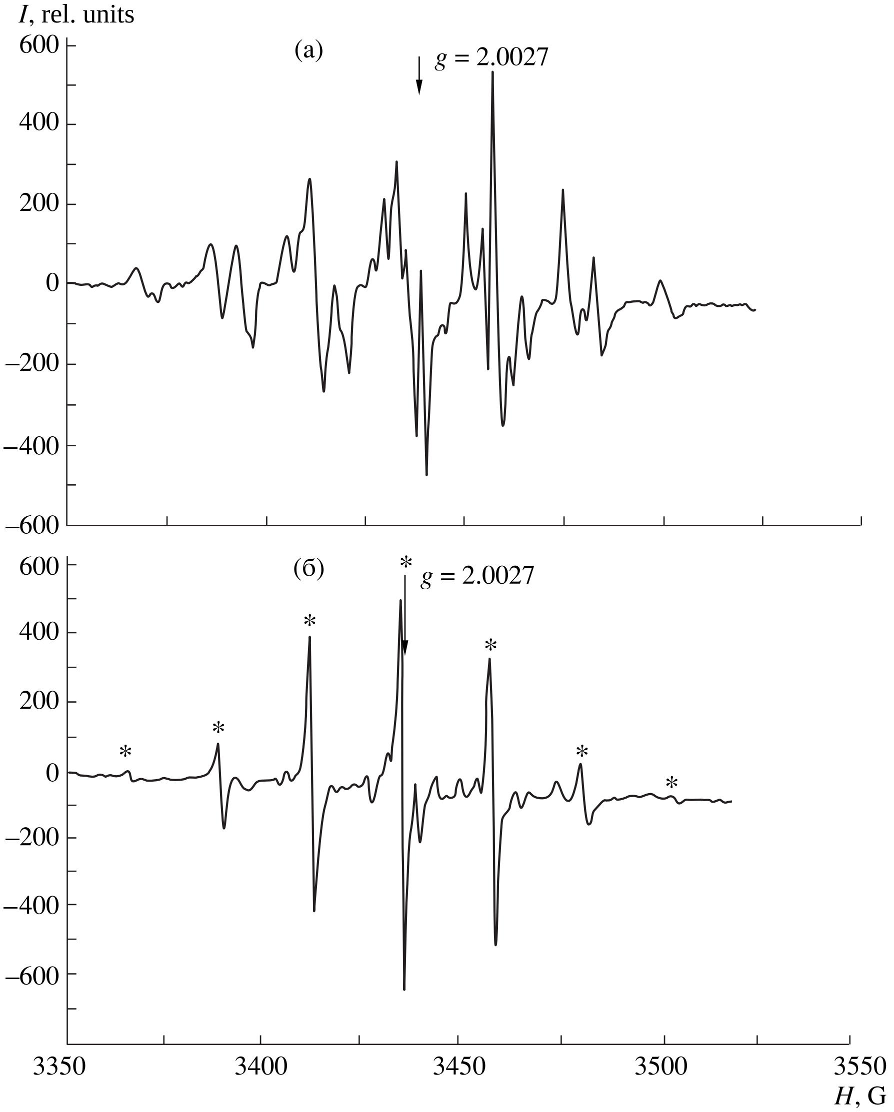


Fig. 4. ESR spectra of radicals (a) $>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$ and (b) $>\mathrm{Si(C^{\bullet}(CH_3)_2)(CH_2{-}CH_3)}$ at 295 K.

radicals decayed and the hydrocarbon radicals $>\mathrm{Si(OH)(CH_2{-}CH_2^{\bullet})}$ were formed in comparable amounts. The ESR spectrum of this radical at 77 K has a characteristic shape: singlet lines are split into doublets associated with the hydrogen atom of the OH group. Thus, the formation of this radical as a product of peroxy radical $>\mathrm{Si(C(O{-}O^{\bullet})(CH_3)_2)(CH_2{-}CH_3)} \longrightarrow >\mathrm{Si(O^{\bullet})(CH_2{-}CH_3)} + \mathrm{O{=}C(CH_3)_2} \longrightarrow >\mathrm{Si(OH)(CH_2{-}CH_2^{\bullet})}$ decomposition points to the fact that the initial radical indeed contains the hydrocarbon fragment C_2H_5.

Based on the obtained experimental data, we conclude that the reaction of radical $>\mathrm{Si(C^{\bullet}(CH_3)_2)(CH_2{-}CH_3)}$ formation is the intramolecular rearrangement of $>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$ that preserves the composition of this radical. This rearrangement can occur as a sequence of two reactions—skeletal isomerization and further hydrogen atom transfer:

$$>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$$

$$\rightleftharpoons >\mathrm{Si(CH(CH_2^{\bullet})(CH_3))(CH_2{-}CH_3)},$$

$$>\mathrm{Si(CH(CH_2^{\bullet})(CH_3))(CH_2{-}CH_3)}$$

$$\longrightarrow >\mathrm{Si(C^{\bullet}(CH_3)_2)(CH_2{-}CH_3)}.$$

We can imagine two different mechanisms of the second step of this process. One of them is the reaction of hydrogen atom transfer from the adjacent carbon atom (1,2-transfer). In this case, an analogous product should have also been seen in the products of the ther-

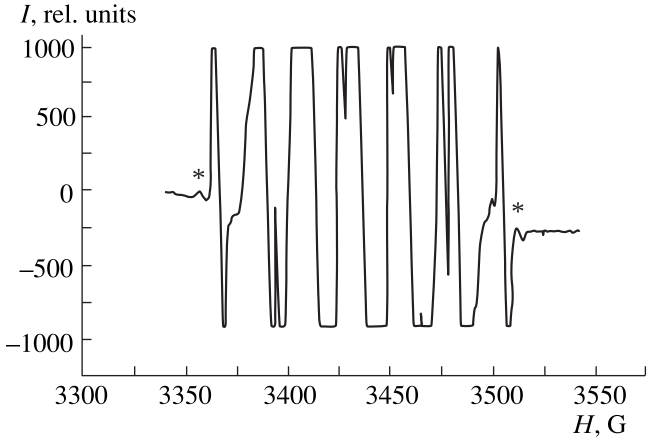


Fig. 5. ESR spectrum of the radical $>\mathrm{Si(O{-}H)(CH_2{-}CH_2^{\bullet})}$ at 295 K. Stars show the satellite lines ^{29}Si.

mal isomerization of the $\equiv\mathrm{Si{-}CH_2{-}CH^{\bullet}{-}CH_3}$ radical. However, when this radical is allowed to stay at 373 K, the product of rearrangement was not registered. The thermal transformations of this radical occurred at >420 K via other pathways.

Kinetic estimates also provide negative evidence for the cited mechanism. The activation energy of hydrogen 1,2-transfer in the hydrocarbon radical of this type is higher than 35 kcal/mol [1]. Therefore, the rate constant of this process at 373 K is lower than 10^{-8} s^{-1}; that is, the rate of this transformation is negligible.

Another mechanism for the hydrogen atom transfer assumes the participation of the second substituent (C_2H_5):

$$>\mathrm{Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} >\mathrm{Si(CH(CH_2^{\bullet})(CH_3))(CH_2{-}CH_3)}, \tag{IV}$$

$$>\mathrm{Si(CH(CH_2^{\bullet})(CH_3))(CH_2{-}CH_3)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} >\mathrm{Si(CH(CH_3)(CH_3))(CH_2{-}CH_2^{\bullet})}, \tag{V}$$

$$>\mathrm{Si(CH(CH_3)(CH_3))(CH_2{-}CH_2^{\bullet})} \xrightarrow{k_3} >\mathrm{Si(C^{\bullet}(CH_3)_2(CH_2{-}CH_3)}. \tag{VI}$$

In this scheme, only reactions of hydrogen atom abstraction from the methyl group are taken into account for process (V), because their constants are much higher than for reactions with the participation of CH_2 groups [3].

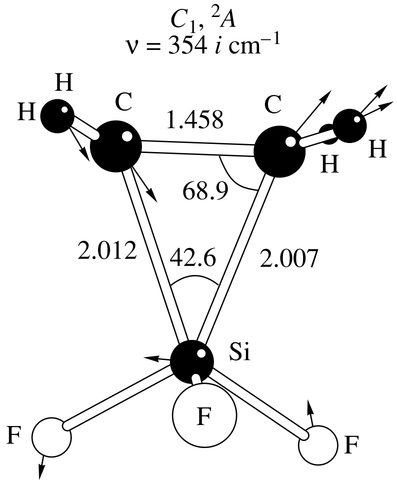
Figure 6 shows the kinetic curve of radical transformation at 373 K in semilogarithmic coordinates. The rate constant determined from the slope of this curve is $k_{\mathrm{app}}(373\ \mathrm{K}) = 3.7 \times 10^{-4}\ \mathrm{s}^{-1}$.

The measured rate constant is apparent, because the considered process does not occur in one step. The upper estimate of the activation energy of skeletal isomerization is obtained assuming that the measured rate constant is k_1. Using the value $A_0 = 10^{12}\ \mathrm{s}^{-1}$, we obtain that the activation energy of this reaction is at most 26.5 kcal/mol.

Based on the available experimental data, we can estimate some of the rate constants from the above scheme. The value $k_2(373\ \mathrm{K}) = 10^2\ \mathrm{s}^{-1}$ is obtained by extrapolating the rate const $k(246\ \mathrm{K}) = (6.6 \pm 0.7) \times 10^{-4}\ \mathrm{s}^{-1}$ of the similar reaction $>\mathrm{Si(CH_2{-}CH_3)(CD_2{-}CD_2^{\bullet})} \longrightarrow >\mathrm{Si(CH_2{-}CH_2^{\bullet})(CD_2{-}CHD_2)}$ assuming that $A_0 = 10^{12}\ \mathrm{s}^{-1}$. This leads us to conclude that the corresponding equilibrium is fast. The value $K_2 = k_2/k_{-2}$ can be set equal to 0.5. It is assumed that the concentrations of radicals $>\mathrm{Si(CH(CH_2^{\bullet})(CH_3))(CH_2{-}CH_3)}$ (**A**) and $>\mathrm{Si(CH(CH_3)(CH_3))(CH_2{-}CH_2^{\bullet})}$ (**B**) in equilibrium is determined by the number of CH_3-group protons from which a hydrogen atom can be abstracted (three for radical **A** and six for radical **B**). If we assume that equilibrium is also established in reaction (IV), then $k_{\mathrm{app}} \approx K_1K_2k_3$. The value of the rate constant k_3 can be estimated using the value of the rate constant $k(295\ \mathrm{K}) = (1.2 \pm 0.1) \times 10^{-4}\ \mathrm{s}^{-1}$ [3] for a similar reaction $>\mathrm{Si(CH_2{-}CH_3)(CH_2{-}CH_2^{\bullet})} \longrightarrow >\mathrm{Si(CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)}$, $k_3(373\ \mathrm{K}) \approx 2.6 \times 10^{-1}\ \mathrm{s}^{-1}$ (A_0 is taken equal $10^{12}\ \mathrm{s}^{-1}$). Then, $K_1(373\ \mathrm{K}) \approx 3.5 \times 10^2$. Assuming that the preexponential factors for k_1 and k_{-1} are similar, the value ΔH for process (IV) is 4.3 kcal/mol.

Information on the activation energy of skeletal isomerization can be obtained from quantum-chemical calculations. The structure of the transition state (TS) for skeletal isomerization of the low-molecular radical $\mathrm{F_3Si{-}CH_2{-}CH_2^{\bullet}}$ ($\mathrm{F_3Si{-}C(1)H_2{-}C(2)H_2^{\bullet}} \rightleftarrows \mathrm{F_3Si{-}C(2)H_2{-}C(1)H_2^{\bullet}}$), which is the simplest model of the studied surface center.

Arrows show the amplitudes and directions of atomic shifts in the transition state. The symmetry and the calculated imaginary frequency of motion along the reaction coordinate are also shown:



The structure of the transition state was optimized using the UMP2/6-31G** method [9]. The thermochemical characteristics of the processes (ΔH(0 K) were calculated at the same level; they are presented in the scheme in kcal/mol):

$$F_3Si^{\bullet} + H_2C{=}CH_2 \longrightarrow F_3Si{-}CH_2{-}CH_2^{\bullet} - 36.0,$$

$$F_3Si{-}C(1)H_2{-}C(2)H_2^{\bullet} \longrightarrow \mathrm{TS} + 19.4$$

$$\longrightarrow F_3Si{-}C(2)H_2{-}C(1)H_2^{\bullet}.$$

Thus, quantum-chemical calculations agree with experimental data and show that the activation energy for the reaction of skeletal isomerization is noticeably lower than the activation energy of radical decomposition with the elimination of an ethylene molecule. Because the energies of transition states are usually overestimated in calculations, the value of the activation barrier for such a process is probably lower than 20 kcal/mol.

To have an idea of the scales of differences on the energies of isomers $>Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)$, $>Si(CH(CH_2^{\bullet})(CH_3))$ $(CH_2{-}CH_3)$, and $>Si(C^{\bullet}(CH_3))_2)(CH_2{-}CH_3)$, we carried out the calculations of model low-molecular radicals $F_3Si{-}CH_2{-}CH^{\bullet}{-}CH_3$, $F_3Si{-}CH(CH_2^{\bullet})(CH_3)$ and $F_3Si{-}C^{\bullet}(CH_3)_2$. Calculations were carried using the density functional theory method [11]. The $F_3Si{-}C^{\bullet}(CH_3)_2$ radical was the most stable. The difference in the ΔH(0 K) values between this radical and the radicals $F_3Si{-}CH_2{-}CH^{\bullet}{-}CH_3$ and $F_3Si{-}CH(CH_2^{\bullet})(CH_3)$ was 2.5 and 7.8 kcal/mol, respectively. Thus, the calculation shows that the isomer containing two methyl groups is more stable. Another important result is that the difference in the heats of formation of radicals $F_3Si{-}CH_2{-}CH^{\bullet}{-}CH_3$ and $F_3Si{-}CH(CH_2^{\bullet})(CH_3)$ is ~5 kcal/mol. This value agrees with the experimental estimate of the difference in the heats of formation of radicals $>Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3)$ and $>Si(CH(CH_2^{\bullet})(CH_3))$ $(CH_2{-}CH_3)$ (ΔH = 4.3 kcal/mol), which was obtained assuming that the reaction of skeletal isomerization occurs under conditions when equilibrium in reactions (IV) and (V) has time to be settled. The obtained result supports this assumption.

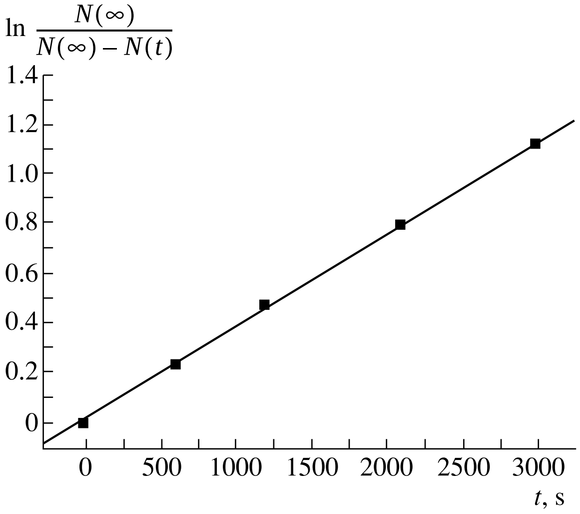


Fig. 6. The kinetic curve of radical $>Si(C^{\bullet}(CH_3)_2)$ $(CH_2{-}CH_3)$ formation in the course of the reaction $>Si(CH_2{-}CH^{\bullet}{-}CH_3)(CH_2{-}CH_3) \longrightarrow >Si(C^{\bullet}(CH_3)_2)$ $(CH_2{-}CH_3)$ (373 K) in the semilogarithmic coordinates ($N(t)$ is time-dependent radical concentration).

Thus, hydrocarbon radicals $(R_1)(R_2)C_{\alpha}^{\bullet}{-}C_{\beta}(R_3)(R_4){-}Si_{\gamma}{\equiv}$, containing a silicon atom as a substituent in the γ-position, can participate in the reaction of skeletal isomerization:

$$\equiv Si_{\gamma}{-}C_{\beta}(2)(R_3)(R_4) - C_{\alpha}^{\bullet}(1)(R_1)(R_2)$$

$$\longrightarrow \mathrm{TS}\left(\equiv Si < \begin{array}{c} \vee \\ C(1) \\ | \\ C(2) \\ \wedge \end{array}\right)$$

$$\longrightarrow \equiv Si_{\gamma}{-}C_{\beta}(1)(R_1)(R_2){-}C_{\alpha}^{\bullet}(2)(R_3)(R_4).$$

Such processes are not typical of hydrocarbon radicals. The reactions of depolymerization, which result in the elimination of the monomer molecule in the cleavage of the $C_{\beta}{-}C_{\gamma}$ bond, are more common to them. The appearance of the new pathway is due to the ability of a silicon atom to participate in reactions with five-coordinated transition states and due to the strengthening of the $C_{\beta}(2){-}Si_{\gamma}$ bond (compared to the $C_{\beta}(2){-}C_{\gamma}$ bond).

The kinetics of isotope exchange (H ⟷ D) in hydrocarbon radicals $>Si(C(1)H_2{-}C(2)H_2^{\bullet})(CD_3)$ and $>Si(C(1)D_2{-}C(2)D_2^{\bullet})(CH_3)$ were studied in [3]. It was shown that even at 373 K, there are no changes in the chemical nature of radicals, and only those processes occur that are associated with the redistribution of H and D atoms. In the case of 1,4-transfer, atoms bound to the terminal carbon atom can only participate in the isotopic exchange. The possibility of the reactions of skeletal isomerization when different hydrogen isotopes are bound to carbon atoms C(1) and C(2) should lead to a new pathway of H(D) atom redistribution in these radicals. This conclusion can be tested experimentally.

ACKNOWLEDGMENTS

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