Russian Chemical Bulletin, Vol. 48, No. 11, November, 1999

Conformation and rotational mobility of ≡SiO$\dot{C}H_2$ radicals grafted onto the silica surface

V. I. Pergushov, E. G. Evtikhieva, and D. A. Tyurin*

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 1854

The conformation of ≡SiOC$^{\cdot}H_2$ radicals was determined by comparison of the ESR data and results of quantum-chemical calculations. Based on the experimental data, the characteristic times (τ_c) of rotational mobility of ≡SiOC$^{\cdot}H_2$ radicals grafted onto a silica surface were estimated over the temperature interval from 77 (τ_c = 15.8 · 10^{-8} s) to 295 K (τ_c = 1.3 · 10^{-8} s).

Key words: grafted radicals, rotational mobility.

Conformation and mobility of radicals grafted onto a silica surface are of interest for analysis of the regularities of many heterogeneous processes. However, the available experimental data are scarce. Using a "bridge" connecting the paramagnetic fragment with the surface of the mineral support, characteristic times of motions of nitroxyl radicals grafted onto the silica surface have previously[1] been determined. At 20 °C, this parameter varies from 1.6 · 10^{-8} to 3.2 · 10^{-8} s, depending on the nature of the "bridge," and the activation energies are 18—24 kJ mol^{-1}. The estimation[2] of the characteristic times of rotational mobility for ≡SiOC$^{\cdot}H_2$ and ≡SiOC$^{\cdot}Me_2$ radicals grafted onto an Aerosil surface at room temperature gave values of 1.3 · 10^{-8} and 2.5 · 10^{-8} s, respectively.

In this work, the ESR data and results of quantum-chemical calculations served to determine the conformation of the grafted ≡SiOC$^{\cdot}H_2$ radical and temperature dependences of the characteristic times of rotational mobility of the radical.

Results and Discussion

Conformation of the ≡SiOC$^{\cdot}H_2$ radical

Molecular conformations of various organosilicon compounds and the chemical and dynamic features of the siloxane bond are well known[3,4]; however, data on the conformation of radicals containing the Si—O—C fragment are scarce. We used the experimental and calculated results of the present work and available published data to estimate the parameters that determine the conformation of this radical.

The shape of the ESR spectrum of the ≡SiOC$^{\cdot}H_2$ radical recorded at 77 K (Fig. 1, *a*) unambiguously indicates axial symmetry the of g tensor and HFC tensor of the paramagnetic species under study. The HFC tensor determined from this spectrum has the following values: $|A_\perp|$ = 57.4 MHz and $|A_\parallel|$ = 52.5 MHz. It is known[5] that the HFC tensor for the α-proton in the >C$^{\cdot}$—H fragment does not possess axial symmetry: $T_{xx} \approx -30$ MHz, $T_{yy} \approx -90$ MHz, and $T_{zz} \approx -60$ MHz (the *X* axis is directed along the C—H bond, the *Z* axis coincides with the symmetry axis of the p-orbital of a unpaired electron). The experimentally observed axial symmetry of the HFC tensor in the ≡SiOC$^{\cdot}H_2$ radical indicates averaging of the T_{xx} and T_{yy} components. It can be assumed that this occurs due to rotation of the —C$^{\cdot}H_2$ fragment about the Si—O bond.

Experimental data on the barriers of internal rotation about the Si—O bond for carbon-centered radicals are scarce. The activation energies of rotation about the Si—O bond in monoalkoxysilane molecules[4] depend on the angle between the Si—O—C bonds and do not exceed 4.5 kJ mol^{-1}. For example, for F_3SiOMe (see Ref. 6), the angle between the Si—O—C bonds is equal to 132°, and the activation energy of rotational mobility about the Si—O bond is 1.65 kJ mol^{-1}. Data of Raman spectroscopy[7] and quantum-chemical calculations[8] obtained for the silyl group in disiloxane and electron diffraction data[9] related to the trimethylsilyl group in hexamethyldisiloxane indicate that the potential barriers for internal rotation of these groups vary from 0 to 0.1 kJ mol^{-1}. Since the barriers of internal rotation about the Si—O bond are low, the assumption about averaging of the T_{xx} and T_{yy} components of the HFC tensor due to rotation of the —C$^{\cdot}H_2$ fragment about the Si—O bond at 77 K is valid.

According to the previously published data,[10] the activation energy of rotational mobility of the methylene fragment of the –CH_2—O—C$^{\cdot}H_2$ radical in γ-irradiated polyoxymethylene is close to 5 kJ mol^{-1}. The barrier of rotation of the peroxide groups in the terminal peroxide radicals in Teflon[11] and that of the

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2092—2095, November, 1999.

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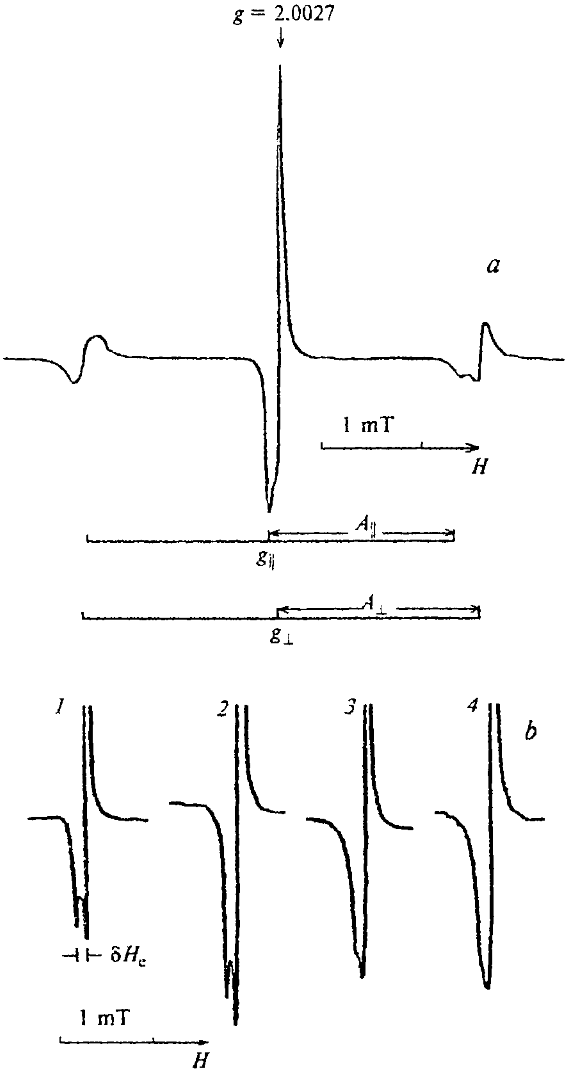

Fig. 1. *a*, ESR spectrum of $\equiv SiOC^{\cdot}H_2$ radicals grafted onto an Aerosil surface recorded at 77 K; *b*, shape of the lower part of the central component of the ESR spectrum at 140 (*1*), 160 (*2*), 180 (*3*), and 200 K (*4*).

fluoroethyl radicals stabilized in an argon matrix[12] do not exceed 1.05 kJ mol^{-1}. At the same time, the barrier of rotation of the methylene groups in the $-CH_2-O-C^{\cdot}H_2$ radical is lower than those of methyl groups in molecules: for example, the barrier of rotation of the methyl group about the C—O bond in dimethyl ether is equal[13] to ~11.4 kJ mol^{-1}.

Taking into account that the experimental data[5] lead to an angle of 116±5° for the $HOOCC^{\cdot}H_2$ radical, we may assume that the H—C—H angle in the $-C^{\cdot}H_2$ radical fragment is approximately equal to 116°. Taking this angle for the $-O-C^{\cdot}H_2$ fragment and assuming that the conformation for which the Si—O bond is projected on the bisector of the H—C—H angle is the optimum conformation of the radical for rotation around the Si—O bond, we optimized the other parameters characterizing the conformation of the $R_3SiOC^{\cdot}H_2$ radicals (R = $(HO)_3SiO$ or F) by the semiempirical PM3 method, determined the spin density of an unpaired electron in s-orbitals of protons of the methylene group, and in this way calculated the surfaces of potential energy of the radicals for different rotation angles about the Si—O and C—O bonds.

The structures were chosen from the following considerations. It is known[4] that in organosilicon compounds the electron-donor or electron-acceptor properties of substituents at the silicon atom have a substantial effect on the conformation of the molecules and dynamic parameters of the siloxane bond, *i.e.*, on the force constants for different types of vibrations of this bond. The $((HO)_3SiO)_3Si$ and F_3Si fragments were used as models for approximate description of the surface silicon atom, because the F_3Si fragment is the most adequate in quantum-chemical calculations for description of the surface silicon atom in the silica lattice.[14]

The results of calculations characterizing the optimized conformations of the $R_3SiOC^{\cdot}H_2$ radicals and the surface of potential energy are almost identical. It is established that the angle between the C—O bond and the CHH plane is ~132°, the Si—O—C and O—C—H angles are equal to ~118° and ~113°, respectively, and the spin densities of a lone electron in the hydrogen s-orbitals are equal to ~0.041. This results in an isotropic HFC constant for protons of 58.5 MHz (~20.9 G),* and the energy barriers of rotation of the fragments of the radical about the Si—O and C—O bonds are equal to ~1 and ~7 kJ mol^{-1}, respectively.

Assuming that the temperature dependence of the rotation frequencies (ν) of the fragments about the bonds in the radical can be presented as $\nu = \nu_0 \exp(-E/RT)$ ($\nu_0 \approx 10^{12}$ s^{-1}, *E* is the energy barrier of rotation), we can estimate the rotation frequencies about the Si—O and C—O bonds at 77 and 295 K. They are equal to ~$2 \cdot 10^{11}$ s^{-1} and ~$3 \cdot 10^{7}$ s^{-1} at 77 K and

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* For the $F_3SiOC^{\cdot}H_2$ radical, we performed the complete optimization of the geometry and solved the electron problem in terms of the unrestricted Hartree—Fock method (UHF/6-311g***//UHF/6-311g***). The following parameters of the thus optimized geometry of the radical were obtained: Si—O, O—C, and C—H bond lengths are equal to 1.585, 1.362, and 1.074 Å, respectively; H—C—H, Si—O—C, and O—C—H angles are 120.9, 135.3, and 115.4°, respectively; the angle between the HCH plane and the C—O bond is equal to 146.8°, and the dihedral Si—O—C—H angles are 105.7°; the isotropic HFC constant was determined by the standard method based on the known value of the *S* wave function calculated by the self-consistent field method, and at the point of the nucleus of the neutral atom it was ~92.1 MHz. The calculations confirmed the assumption on the optimum conformation of the radical for rotation of the methylene fragment about the Si—O bond; however, the isotropic HFC constant obtained for protons substantially exceeds the experimental value (~55.8 MHz or ~19.9 G).

$\sim 4 \cdot 10^{11}$ s^{-1} and $\sim 7 \cdot 10^{10}$ s^{-1} at 295 K. This implies that for recording the ESR spectrum, rotation about the Si—O bond at both temperatures should be considered free, rotation about the C—O bond at 77 K should be absent, whereas that at 295 K should be free. This result is completely consistent with the spectroscopic experiment.

To establish adequacy of the "optimized" geometry of the radical to the parameters of the experimentally detected ESR spectra, we calculated the HFC tensor for rotation of the fragment of the radical only about the Si—O bond (77 K) and for rotation of the fragments of the radical about the Si—O and C—O bonds (at 295 K) using the angles between the bonds of the "optimized" conformation. To achieve the best agreement between the calculated values and those determined from the ESR spectrum (77 K) for the HFC tensor of the $\equiv$SiOC$^{\cdot}$H$_2$ radical ($|A_{\perp}|$ = 57.4 MHz, $|A_{\parallel}|$ = 52.5 MHz) and isotropic HFC constant (A_{iso} = 55.8 MHz), we changed only the value of the Si—O—C angle, which in monoalkoxysilanes can vary from 120 to 132°. In the calculations for the $\equiv$SiOC$^{\cdot}$H$_2$ radical, we used the main values of the components of the HFC tensors of protons, which are equal to the mean values of the corresponding components for the HOOCC$^{\cdot}$H$_2$ radical and were reduced to the ratio 55.8/61 ≈ 0.915. The value of 55.8 MHz is the isotropic HFC constant on protons of the $\equiv$SiOC$^{\cdot}$H$_2$ radical $A_{\text{iso}} = (2|A_{\perp}| + |A_{\parallel}|)/3 = (2 \cdot 57.4 + 52.5)/3$, and the value of 61 MHz is the mean value of isotropic HFC constants on protons of the HOOCC$^{\cdot}$H$_2$ radical[6,7]: $T_{zz} = -0.915(55 + 59)/2 = -52.2$ MHz, $T_{yy} = -84.6$ MHz, and $T_{xx} = -30.7$ MHz. It was shown that the geometry of the radical optimized by the UHF method corresponds best to the experimental data. For example, when the fragments of the radical rotate only about the Si—O bond (77 K), the best agreement between the experimental ($|A_{\perp}|$ = 57.4 MHz, $|A_{\parallel}|$ = 52.5 MHz) and calculated data ($A_{\perp} = -57.3$ MHz, $A_{\parallel} = -53.0$ MHz) were obtained for a Si—O—C angle of 133° (the angle calculated by the UHF method is equal to 135°). Under the assumption of rotation of the fragments of the radical in all three directions (295 K), the best agreement between the experimental ($|A_{\text{iso}}|$ = 55.8 MHz) and calculated data ($A_{\text{iso}} = -55.8$ MHz) was obtained for a Si—O—C angle equal to 135°. Similar data for the geometry of the radical optimized by the PM3 method were obtained only under the assumption that for rotation of the fragments of the radical only about the Si—O bond, the Si—O—C angle is equal to 125°, and for rotation of the fragments of the radical in all three directions, this angle amounts 126°. At the same time, the Si—O—C angle calculated by the PM3 method is equal to 119°.

Rotational mobility of the $\equiv$SiOC$^{\cdot}$H$_2$ radical

Figure 1, *b* shows how increase in temperature affects the shape of the lower part of the central component of the ESR spectrum of the $\equiv$SiOC$^{\cdot}$H$_2$ radical, *i.e.*, the component for which the total spin of protons of the radical is equal to zero. It can be seen that as the temperature increases the difference $\delta H_e = H_{\perp} - H_{\parallel}$ decreases, indicating a decrease in the characteristic time of rotational mobility τ_c of the grafted radical.

Based on the experimental data obtained and using the previously described method,[15] we estimated τ_c for the $\equiv$SiOC$^{\cdot}$H$_2$ radicals:

$$\tau_c = \{2^{-1/2}\gamma_e[(\delta H_0)^2 - (\delta H_e)^2]^{1/2}\}^{-1}, \qquad (1)$$

where γ_e is the gyromagnetic ratio of a free electron ($\sim 1.76 \cdot 10^3$ rad s^{-1} T^{-1}), and δH_0 and δH_e are the distances between the lines in the absence or presence of intertransformations between parallel and perpendicular orientations of the radical. δH_0 was determined from the temperature dependence of δH_e under the assumption that $\delta H_0 = \lim \delta H_e$ at $T \rightarrow 0$. We obtained $\delta H_0 \approx 0.137$ mT (Fig. 2). The data obtained which illustrate the temperature dependence of τ_c are presented in Table 1.

The dependence of $\ln v \equiv \ln(1/\tau_c)$ on $1/T$ substantially deviates from linearity (Fig. 3). The effective activation energies E of rotational mobility of the radical

Table 1. Characteristic time (τ_c) of rotational mobility of the $\equiv$SiOC$^{\cdot}$H$_2$ radical at different temperatures

T/K	$\tau_c \cdot 10^8$/s	$v^* \cdot 10^{-7}$/s^{-1}
77	15.8	0.63
140	8.9	1.1
160	8.0	1.3
180	6.4	1.6
200	6.0	1.7
295**	1.3**	7.7**

* $v = 1/\tau_c$. ** Ref. 2.

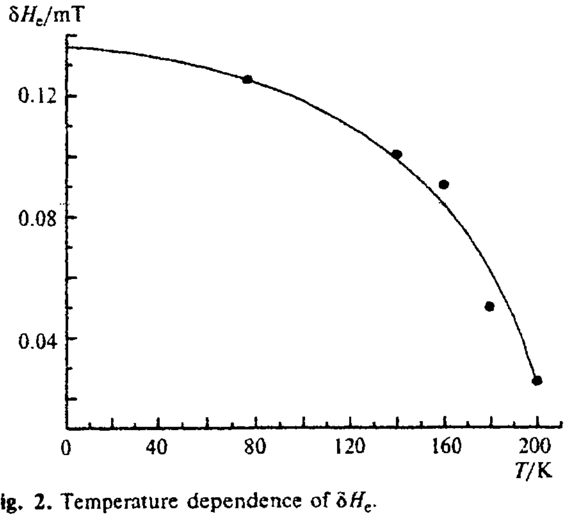

Fig. 2. Temperature dependence of δH_e.

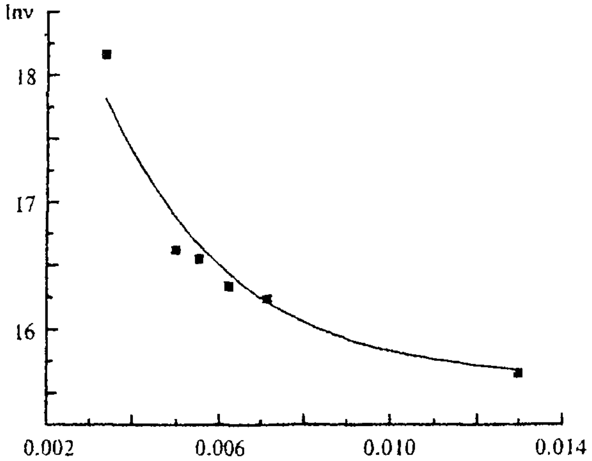

Fig. 3. Temperature dependence of rotational mobility (correlation time $\tau_c = 1/\nu$) of $\equiv$SiOC$^{\cdot}$H$_2$ radicals in the coordinates of the Arrhenius equation.

determined from the tangent slope of the lnv versus $1/T$ plot are equal to ~0.2 kJ mol^{-1} (77 K) and ~6 kJ mol^{-1} (295 K).

In our opinion, the increase in the effective activation energy for rotational mobility of the radical with temperature increase is due to an increase in the contributions to the rotational mobility of the grafted radical of rotation of the methylene group about the C—O bond and deformation vibrations of the Si—O—C angle. It can be assumed that our estimations of the activation energies of rotational mobility of the radical at 77 and 295 K are the upper limit of the activation energy of rotation about the Si—O bond (~0.2 kJ mol^{-1}) and the lower limit of the activation energy of rotation about the C—O bond (~6 kJ mol^{-1}) in the $\equiv$SiOC$^{\cdot}$H$_2$ radical.

Thus, in this work, based on the experimental data and results of quantum-chemical calculations, we established the conformation and estimated the molecular mobility of $\equiv$SiOC$^{\cdot}$H$_2$ radicals grafted onto an Aerosil surface over a wide temperature range.

The authors thank A. L. Buchachenko for fruitful advice and discussion of the work and V. A. Radtsig for valuable remarks concerning the results of Ref. 16 that stimulated writing of this article.

The work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33662) and Federal Target Program "Integration" (Project No. K0093).

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Received November 4, 1998;
in revised form May 25, 1999