Chemical dynamics of $\equiv SiOC^{\bullet}O$ radicals grafted on the activated silica surface

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The chemical dynamics of $\equiv SiOC^{\bullet}O$ radicals grafted on the silica surface was studied in the 77—290 K temperature interval. The rotation diffusion coefficients and characteristic times of rotational mobility of the radicals were estimated.

Key words: grafted radicals, rotational mobility, silica.

Studies of the mobility of radicals grafted on the surface of a mineral support provide information on the local environment of paramagnetic species. The mobility or intensity of rotational motion of radicals is usually characterized by the correlation time τ, frequency $\nu = \tau^{-1}$, and rotation diffusion coefficient $D = (6\tau)^{-1}$.

Paramagnetic probes and labels are usually used for studying the chemical dynamics of molecules in liquids and polymers and on solid surfaces, whereas data on the chemical dynamics of radicals grafted on a solid surface are scarce. The characteristic times and activation energy of the rotational mobility of nitroxyl radicals grafted on the SiO_2 surface by "bridges" with different lengths have previously been obtained.[1] The τ values range from $1.6 \cdot 10^{-8}$ to $3.2 \cdot 10^{-8}$ s at 20 °C, depending on the length of the "bridge," and E_a = 18—24 kJ mol^{-1}. For the $\equiv SiOC^{\bullet}H_2$ and $\equiv SiOC^{\bullet}Me_2$ radicals on the activated Aerosil surface at room temperature, the τ values are $1.3 \cdot 10^{-8}$ and $2.5 \cdot 10^{-8}$ s, respectively.[2] Comparison of the results of quantum-chemical calculations and ESR spectroscopy data made it possible to establish[3] the conformation of the $\equiv SiOC^{\bullet}H_2$ radicals grafted on the SiO_2 surface and conclude that the rotational mobility of the radical can be retarded by its interaction with the potential field of the activated surface.

In this work, we studied the chemical dynamics of $\equiv SiOC^{\bullet}O$ radicals grafted on the Aerosil surface in a wide temperature range.

Experimental

Aerosil A-175 was used. The $\equiv SiOC^{\bullet}O$ radicals were generated by the interaction of $\equiv SiO^{\bullet}$ radicals (obtained by photochemical activation of the Aerosil surface) with CO from the gas phase at room temperature and CO pressure of ~1 N m^{-2}. The procedure of the photochemical activation of the Aerosil surface has been described previously.[4] This method of Aerosil surface activation also gives a minor amount of silyl radicals $\equiv Si^{\bullet}$ (Fig. 1, *a*, *b*). However, their interaction with CO is reversible, and at ~300 K and a CO pressure of <133 N m^{-2} the equilibrium is almost completely shifted toward the starting reactants.[5] Since after the interaction of CO with the $\equiv SiO^{\bullet}$ and $\equiv Si^{\bullet}$ radicals the sample was evacuated at room temperature to a pressure ≤1 N m^{-2}, we believe that at least 95% of the total number of paramagnetic centers are $\equiv SiOC^{\bullet}O$ radicals.

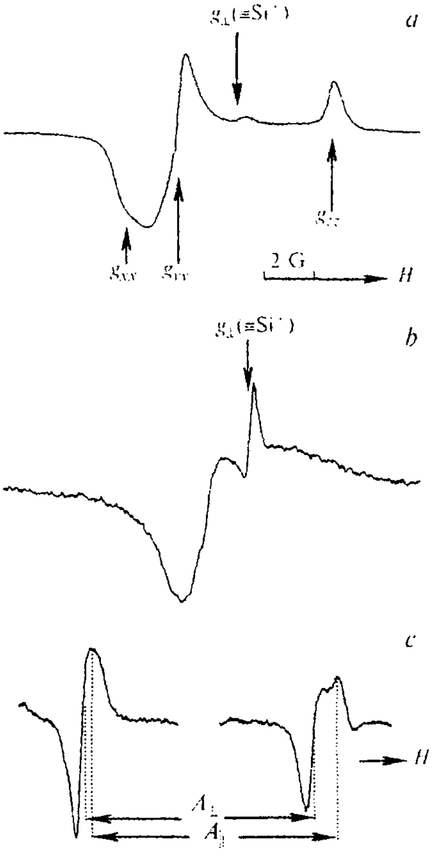

Fig. 1. ESR spectra of $\equiv SiOC^{\bullet}O$ (*a*, *b*) and $\equiv SiO^{13}C^{\bullet}O$ (*c*) radicals recorded at 77 (*a*, *c*) and 295 K (*b*).

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ESR spectra in the X-range were recorded on an E-3 radiospectrometer (Varian) with a high-frequency modulation of 100 kHz under conditions excluding saturation and modulation broadening. To determine the components of the g tensor as reference points, we used the known effective values of the g factors for the third and fourth HFS components of diamagnetically diluted Mn^{2+} ions in MgO: $g_3 = 2.0328 \pm 0.0001$ and $g_4 = 1.9812 \pm 0.0001$, the value between them being $\Delta H_{3-4} = 86.76 \pm 0.05$ G at 20 °C (data from the All-Union Research Institute of Physicotechnical and Radio Engineering Measurements); and $g_\perp = 2.00055$ for the silyl radical $(\equiv SiO)_3Si^{\cdot}$.[6] ESR spectra were recorded at different temperatures in a Dewar tube placed directly into the radiospectrometer cavity. The temperature was maintained with an accuracy of ±1 °C using an E-4557-9 attachment (Varian).

Results and Discussion

Conformation of radical ≡SiOC˙O. The line shape in the ESR spectrum of the ≡SiOC˙O radical recorded at 77 K (see Fig. 1, *a*) indicates a triaxial anisotropy of the g tensor. The effective values of the components of the g tensor were determined by the positions of the characteristic points in the ESR spectrum at 77 K ($g_{xx} = 2.0032 \pm 0.0002$, $g_{yy} = 2.0020 \pm 0.0001$, and $g_{zz} = 1.9984 \pm 0.0001$), which agree satisfactorily with the previously determined analogous values[7]: 2.0031, 2.0012, and 1.9977, respectively. The spectrum of the radical at room temperature (see Fig. 1, *b*) is not isotropic; therefore, it is impossible to estimate the isotropic g factor with good accuracy.

Based on comparison of the experimental data and results of semiempirical calculations by the density functional theory taking into account the p- and d-orbitals (the DFT method in the PBE approximation), we described the configuration of the ≡SiOC˙O radical grafted on the Aerosil surface. The main criterion for comparison of the calculated and experimental data was the isotropic HFC constant a_{iso} on the ^{13}C nuclei determined from the spectrum of the $\equiv SiO^{13}C^{\cdot}O$ radical (see Fig. 1, *c*): $a_{iso} = (2A_\perp + A_\parallel)/3 = (2 \cdot 218 + 215)/3 \approx 216$ G. To represent the surface Si atom in the SiO_2 lattice, we used[8] the F_3Si fragment in quantum-chemical calculations. The calculated HFC constant with the ^{13}C nucleus in the $F_3SiOC^{\cdot}O$ radical with a conformation corresponding to its minimum energy agrees satisfactorily with the experimental value (Table 1).

Table 1. Structural parameters of $F_3SiOC^{\cdot}O$ radicals and the HFC constant on the ^{13}C nuclei calculated by the density functional theory

Parameter	Value
Bond length/Å	
Si—O	1.67
O—C	1.37
C=O	1.18
Angle/deg	
Si—O—C	123
O—C—O	127
Si—O—C—O	0
a_{iso}/G	207

Rotational mobility of radical ≡SiOC˙O. The ESR spectra at ~120 K exhibit transformation from the triaxial g tensor to that with axial symmetry (Fig. 2), which indicates the almost complete averaging of the x and y components of the g tensor, occurring, in our opinion, because of the rotation of the radical fragment about the Si—O bond. The band assigned to torsional vibrations of the molecular fragments about the siloxane bond in the alkylsiloxane molecules in the gas phase lies[9] in the region of 80—100 cm^{-1}; hence, we accept the pre-exponential factor $\nu_0 \approx 10^{12}$ s^{-1}. Taking into account that the frequency of averaging vibrations should be at least equal to $\nu_{aniso} = |(g_{xx} - g_{yy})/g| \cdot 9.5 \cdot 10^9 \approx 6 \cdot 10^6$ s^{-1} ($g = 2.00$, $9.5 \cdot 10^9$ is the microwave frequency of the radiospectrometer), we can estimate the activation energy of such a motion as ≤12 kJ mol^{-1}.

When the temperature increases from 77 to 239 K, the lines are broadened and draw together (see Fig. 2), which is due at first to averaging of the g_{xx} and g_{yy} components (below ~120 K) and then to averaging of the parallel ($g_\parallel = g_{zz}$) and perpendicular ($g_\perp = (g_{xx} + g_{yy})/2$) components of the g tensor. The changes found in the

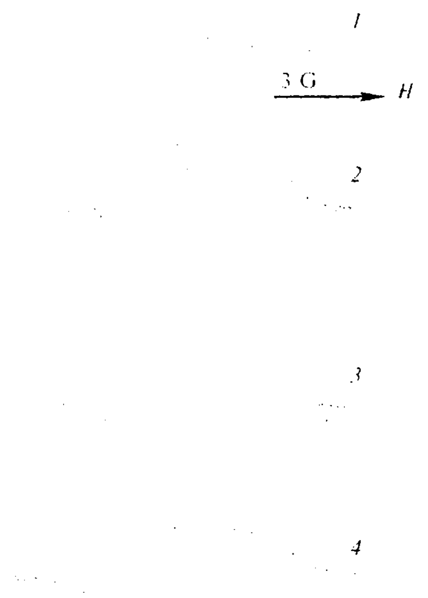

Fig. 2. Simulation of the ESR spectra of ≡SiOC˙O radicals recorded at 77 (*1*), 129 (*2*), 151 (*3*), and 239 K (*4*). The experimental spectra, line; calculation, points.

spectra are stipulated by an increase in the intensity of the thermal motion of the grafted radicals with temperature increase.

The rotation mobility of the radicals was quantitatively characterized by two methods. The first of them is based on the adaptation of the equation[10] for calculation of the characteristic mobility time of radicals with axial symmetry of the *g* tensor, as it has been done previously[3]:

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

where $\gamma = 1.76 \cdot 10^7$ rad s^{-1} G^{-1} is the gyromagnetic ratio for a free electron, and δH_0 and δH_e are the distances between the lines (in magnetic field strength units) in the absence and presence of mutual transformations of radicals with parallel and perpendicular orientations of their magnetic moments, *i.e.*, $\delta H_e = H_{\parallel} - H_{\perp}$.

A disadvantage of this method of estimation of τ is the necessity to know the value of δH_0. Meanwhile, in our case the partial averaging of the Zeeman interaction anisotropy due to the rotation of the grafted radical cannot be excluded even at 77 K. To calculate the characteristic time τ of the rotational motion of the radical, we used the value of $\delta H_0 \approx 3385[0.5(g_{xx} + g_{yy}) - g_{zz}]/2.00055 \approx 7.1$ G (for specific experimental conditions, we may accept with good accuracy that $gH \approx 6771.9$). We assumed that at 77 K the averaging of the components of the *g* tensor is insignificant as compared to the difference $0.5(g_{xx} + g_{yy}) - g_{zz}$.

The second method is the determination of the rotation diffusion coefficient *D* by comparison of experimental ESR spectra recorded at different temperatures with the calculated spectra. The experimental ESR spectra were simulated by the nonlinear least-squares method using the Freed simulation program (version 1.6)[11]* under the assumption of Brownian radical motion. The initial approximation was the components of the *g* tensor and the individual linewidth found from the experimental spectrum recorded at 77 K. The components of the *D* tensor (rotation diffusion tensor), angles determining the mutual orientation of the *g* and *D* tensors (Euler angles), and parameters characterizing the individual line shape could be variables in simulation. Analysis of the correlation matrices obtained by computer simulation of the ESR spectra and visual comparison of the experimental and calculated spectra suggested that the experimental spectra should be simulated under the assumption of axial symmetry of the *D* tensor and at unchanged Euler angles. Since the dihedral Si—O—C—O angle in the $F_3SiOC^{\cdot}O$ radical is equal to 0° (see Table 1), the angle between the *z* components of the *g* tensor and the rotation diffusion tensor is the most important, being equal to ~17° in our experiments.

Table 2. Rotation diffusion coefficients and characteristic times of the rotational mobility of $\equiv SiOC^{\cdot}O$ radicals

T/K	$D \cdot 10^{-6}/s^{-1}$			$\tau \cdot 10^8/s$	
	$D_{\perp}$	$D_{\parallel}$	D_{av}	I*	II**
129	0.36	5.1	1.94	8.59	2.78
140	0.31	5.6	2.07	8.04	2.36
151	0.95	7.1	3.0	5.56	2.47
162	1.21	6.5	2.97	5.60	2.05
173	1.57	6.3	3.15	5.30	2.05
184	1.92	6.1	3.31	5.03	1.89
195	1.89	6.1	3.29	5.06	1.80
206	2.91	4.1	3.31	5.04	1.78
217	3.31	3.2	3.27	5.09	1.77
228	4.42	3.9	4.25	3.92	1.67
239	4.49	4.0	4.33	3.85	—

* Determined from the average diffusion coefficient $\tau = [6(2D_{\perp} + D_{\parallel})/3]^{-1}$.

** Calculated by formula (1).

Thus, in calculations we varied the dynamic parameters (the rotation diffusion coefficients $D_{\parallel}$ and $D_{\perp}$) and used the most general forms of the shape of the individual line, *viz.*, the convolution of the Lorentzian and Gaussian functions. The simulation of the spectra at different temperatures is presented in Fig. 2.

The τ values calculated by formula (1) and obtained by computer simulation of the ESR spectra using the well-known program[11] differ 2.5—3.5-fold. The results indicate that the characteristic times calculated by formula (1) can be used as satisfactory estimates of the rotational mobility of radicals.

The values of rotation diffusion coefficients indicate the existence of at least two types of motions participating in the averaging of the anisotropic Zeeman interaction in the $\equiv SiOC^{\cdot}O$ radical. In addition, despite the calculated and recorded at 77 K spectra coinciding unsatisfactorily, it is seen that even at this temperature the radicals retain a high mobility ($D_{\parallel}$ and $D_{\perp}$ are $\sim 3 \cdot 10^6$ and $\sim 2 \cdot 10^5$ s^{-1}, respectively). The plots of $\ln D_i$ (D_i is $D_{\parallel}$ or $D_{\perp}$) *vs* inverse temperature (Fig. 3) give the activation energies of the types of motions characterized by the corresponding rotation diffusion coefficients of the radicals, which are equal to ~0 and 6.3 kJ mol^{-1}. The last value can be attributed to rotation of the grafted radical about the Si—O bond. It is known that the rotation barrier of SiR_3 groups (R = H, Cl, and Me) in alkylsiloxane molecules in the gas phase about the siloxane bond is very low (≤5.4 kJ mol^{-1})[14—17] due to the specific structure of the siloxane bond, and the Si—O—C angle can vary in wide intervals from 121° to 132°. The transformation of the ESR spectrum of the radical with the triaxial *g* tensor into that with the axial-symmetry *g* tensor found by us at 120 K results in a rotation activation energy of ≤12 kJ mol^{-1}, which does not contradict the data presented above.

However, complete averaging of the Zeeman interaction anisotropy was not found in the ESR spectra of the

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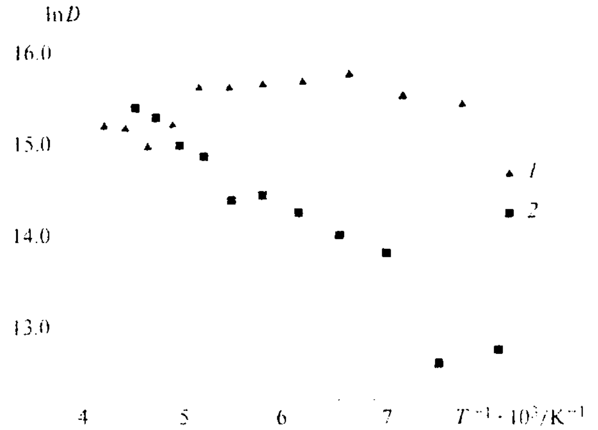

Fig. 3. Temperature plots of the rotation diffusion coefficients $D_{\parallel}$ (*1*) and $D_{\perp}$ (*2*) in the Arrhenius coordinates.

$\equiv\mathrm{SiOC^{\cdot}O}$ radicals in the whole temperature range: at 290 K $\delta H_{\mathrm{e}} \approx 2$ G. Possible motions resulting in the incomplete averaging of the *g* factor anisotropy can be deformational vibrations of the Si—O—C angle or torsional vibrations about the O—C bond (changes in the dihedral Si—O—C—O angle) with the amplitudes depending on the thermal motion energy. These motions do not require overcoming of the activation barrier because they occur near the minimum of the potential surface, but their amplitudes are restricted by intraradical interactions and, most likely, by interaction of the radical with the potential field of the surface. In our opinion, such motions cannot completely average the *g* factor anisotropy.

Thus, in this work, we estimated the rotation diffusion coefficients in the temperature range of 77—240 K and suggested the character of the motions resulting in the partial averaging of the Zeeman interaction anisotropy for the $\equiv\mathrm{SiOC^{\cdot}O}$ radical grafted on the activated Aerosil surface.

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