

Free Radical Reactions of N₂O Molecules

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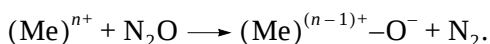
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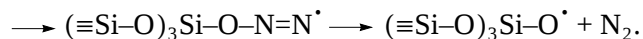
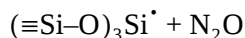
Abstract—Experimental data are presented on the spectral (ESR, IR, and optical) and thermochemical characteristics of a complex between the $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet$ radical and an N₂O molecule. The rate constants of separate reactions in the systems $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet + \text{N}_2\text{O}$ and $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet + \text{N}_2\text{O}$ are found. The results of quantum chemical calculations of potential energy surfaces and spectral characteristics are presented for the following systems: $\text{H}^\bullet + \text{N}_2\text{O}$, $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O}$, $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$, $\text{F}_2\text{HSi}^\bullet + \text{N}_2\text{O}$, $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$, and $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$. The latter three systems served as molecular models for experimentally found systems. Based on experimental and theoretical data, the product of N₂O addition to $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet$ has the structure $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$. The reactions of free radicals $\text{H}^\bullet$, $\text{H}_3\text{C}^\bullet$, $\text{H}_3\text{Si}^\bullet$, $\text{F}_2\text{HSi}^\bullet$, $\text{F}_3\text{Si}^\bullet$, $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet$, and $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ with N₂O are compared. The spectrum of optical absorbance of the $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}^\bullet$ radical is recorded and qualitatively characterized.

INTRODUCTION

The N₂O molecule is a donor of atomic oxygen (the heat of the reaction $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(\text{P})$ is 40 kcal/mol [1]) and it is used to obtain the paramagnetic species like O[•] from the F-sites on various oxide surfaces [2, 3]:



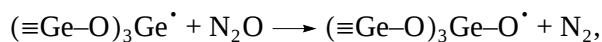
However, only for the system $\equiv\text{Si}^\bullet + \text{N}_2\text{O}$, the intermediate product of this reaction was registered experimentally. The ESR method has been used to register the product of nitrous oxide addition to a silyl-type radical stabilized on the SiO₂ surface [4]. This complex has absorption bands with maxima near 3, 5 and >6 eV [5, 6]. When heated above 350 K, the complex is decomposed. Molecular nitrogen is evolved to the gas phase in an amount comparable with the number of decomposed paramagnetic centers and the $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}^\bullet$ radicals are formed. Based on these data, the structure $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}-\text{N}=\text{N}^\bullet$ was assigned to the complex [4]:



The formation of the intermediate with this structure also seemed preferable due to the high strength of the bond between silicon and oxygen atoms. Then, Chuvylkin *et al.* [7] used the semiempirical quantum chemical calculation scheme CINDORU [8] to calculate the radiospectroscopic characteristics of a complex with a similar structure. Structure optimization was not carried out and the geometry with the “standard” values of bond lengths and valence angles was used [9]. The cal-

culated hyperfine interaction constants of an unpaired electron with the magnetic momentums of two nitrogen atoms were in acceptable agreement with the experimental values. This fact seemed to support the correctness of the proposed chemical structure of the complex.

Bobyshev and Radtsig [10, 11] experimentally studied the oxidation of $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ radicals stabilized on the surface of mechanically activated germanium oxide by nitrous oxide. In that case, the process led to similar final products:



but the intermediate product of N₂O addition to the germanium-centered radical was not registered. Since the germanium–oxygen bond is ~30 kcal/mol weaker in than the silicon–oxygen bond [11], it was assumed that the bond strength is the reason for the disappearance of the local maximum on the potential energy surface corresponding to the metastable complex in the case of the silicon-centered radical.

Free radical reactions with nitrous oxide were studied in the gas phase [12–18]. Recently, several experimental [12–16] and theoretical [14, 19, 20] papers were devoted to the study of the H(D) + N₂O system. The products of this reaction are the hydroxyl radical and molecular nitrogen. The mechanism of this reaction is based on the results of quantum chemical calculations of the potential energy surface for this system. According to these calculations, a hydrogen atom can undergo the addition to a nitrous oxide molecule to form the metastable H–N=N–O[•] radical (the estimated heat of this reaction is 15–20 kcal/mol [14, 19, 20]). Another possible product of hydrogen atom addition to a nitrous

oxide molecule from the side of the oxygen atom is the $\text{H}-\text{O}-\text{N}=\text{N}^\bullet$ radical, which has a structure analogous to the structure of the complex of the silyl radical $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}-\text{N}=\text{N}^\bullet$ [4]. According to quantum chemical calculation, this product is unstable or poorly stable. Until now, the $\text{H}-\text{N}=\text{N}-\text{O}^\bullet$ radical has not been registered. The cited data led us to return to the problems of the mechanism of reactions $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet + \text{N}_2\text{O}$ and $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet + \text{N}_2\text{O}$ and the structure of the discovered nitrous oxide complex with the silicon-centered free radical. This paper presents new experimental data on the spectral characteristics of the complex and on the rate constants of some steps in these systems. The quantum chemical calculations of the potential energy surfaces and the spectral characteristics of the model systems $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$, $\text{F}_2\text{HSi}^\bullet + \text{N}_2\text{O}$, and $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$ are used to interpret experimental data. In addition, three other systems were calculated: $\text{H} + \text{N}_2\text{O}$, $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O}$, and $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$. This made it possible to compare the oxidation reactions of nitrous oxide with different radicals.

The interest in the processes of nitrous oxide is due to environmental problems in the atmosphere. Nitrous oxide, as well as carbon dioxide, are responsible for the greenhouse effect and can play a role in ozone depletion (NO formation in the reaction of nitrous oxide with atomic oxygen $\text{O}(\text{}^1\text{S})$). The $\text{H}-\text{N}=\text{N}-\text{O}^\bullet$ radical is assumed to be the main intermediate in another atmospheric reaction: $\text{O}=\text{N}^\bullet + \text{N}-\text{H}$ [19–21].

1. QUANTUM CHEMICAL CALCULATIONS OF POTENTIAL ENERGY SURFACES AND SPECTRAL CHARACTERISTICS FOR THE SYSTEMS

$\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$, $\text{F}_2\text{HSi}^\bullet + \text{N}_2\text{O}$, $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$,
 $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$, $\text{H} + \text{N}_2\text{O}$, AND $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O}$

In the calculations, the molecular models of radical centers stabilized on the surfaces of SiO_2 and GeO_2 were used. The $\text{F}_3\text{Si}^\bullet$ radical modeled the paramagnetic center $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet$, the $\text{F}_2\text{HSi}^\bullet$ radical modeled $(\equiv\text{Si}-\text{O})_2\text{Si}^\bullet-\text{H}$, and the $\text{F}_3\text{Ge}^\bullet$ radical modeled $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ (see discussion in [22]). The optimization of the structures of molecules, radicals, and transition states for different channels and their transformations was carried out by minimizing the gradient norm using density functional theory (B3LYP/6-311G** [23, 24]). For all optimized structures, vibrational spectra were calculated. The transition states had only one eigenvalue of the Hessian matrix. We also calculated the radiospectroscopic characteristics of radicals: the constants of the isotropic and anisotropic interactions of an unpaired electron with the magnetic momentums of nuclei [25].

For the systems $\text{H} + \text{N}_2\text{O}$, $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O}$, $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$, and $\text{F}_2\text{HSi}^\bullet + \text{N}_2\text{O}$, the energies of structures optimized at the DFT level were also calculated using the G2MP2 method [26] (one-point calculations). This method was developed for calculating the heats of formation of compounds and usually gives better estimates of thermochemical characteristics of reactions than DFT. The results of calculating the formation heats at 0 K at the G2MP2 level for the $\text{F}_2\text{HSi}^\bullet + \text{N}_2\text{O}$ system was used to introduce an empirical correction to DFT results for the $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$ and $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$ systems: $\Delta H_{\text{corr}} = \Delta H(\text{DFT}) + [\Delta H_{\text{F}_2\text{HSi}}(\text{G2MP2}) - \Delta H_{\text{F}_2\text{HSi}}(\text{DFT})]$. When comparing experimental and theoretical data for the model systems, corrected values were used.

The results of quantum chemical calculations of the partition functions (vibrational partition functions were calculated in the harmonic approximation) were used to estimate the preexponential factors of mono- and bimolecular reactions on solid surfaces. According to absolute rate theory, the rate constant k of the process $\text{A} + \text{B} \rightarrow (\text{AB})^* \rightarrow \text{products}$ $k = k_0 \exp(-E_a/RT) = (kT/h)(Z^*/Z_A Z_B) \exp(-E_a/RT)$, where Z^* , Z_A , and Z_B are the partition functions for the transition state and reactants, and E_a is the activation energy [27]. For center A that modeled a surface center and for transition state $(\text{AB})^*$, only the vibrational partition function was taken into account. All quantum chemical calculations were carried out using Gaussian 94 [28].

The results of energy calculations for optimized structures, their zero-point energies, and the relative enthalpies of formation at 0 K are shown in Table 1.

Figure 1a shows the structure of the product of nitrous oxide addition to the $\text{F}_3\text{Si}^\bullet$ radical (C_s symmetry and the ${}^2\text{A}'$ state). All attempts to find the local minimum on the potential energy surface corresponding to the addition of nitrous oxide to the silyl radical via the oxygen atom failed. In this mutual arrangement of the radical center and nitrous oxide, the O–N bond is elongated and cleaved to form an oxy radical and a nitrogen molecule as the distance between silicon and oxygen atoms becomes close to the length of a chemical bond.

Table 2 shows the results of calculations of the vibrational spectrum of this radical. Rotation around the Si–N bond has a very low frequency of 30 cm^{-1} . According to the calculation, the height of the activation barrier that separates equivalent equilibrium positions of the radical is as low as 0.14 kcal/mol (see Fig. 2, curve 1). Therefore, at ordinary temperatures, this motion can be considered as free rotation.

The potential barrier for the rotation around the N–N bond in the radical is noticeably higher. A change in the SiNNO torsion angle by 30° (from an equilibrium value of 180° to 150°) resulted in an increase in the system energy by 2.5 kcal/mol .

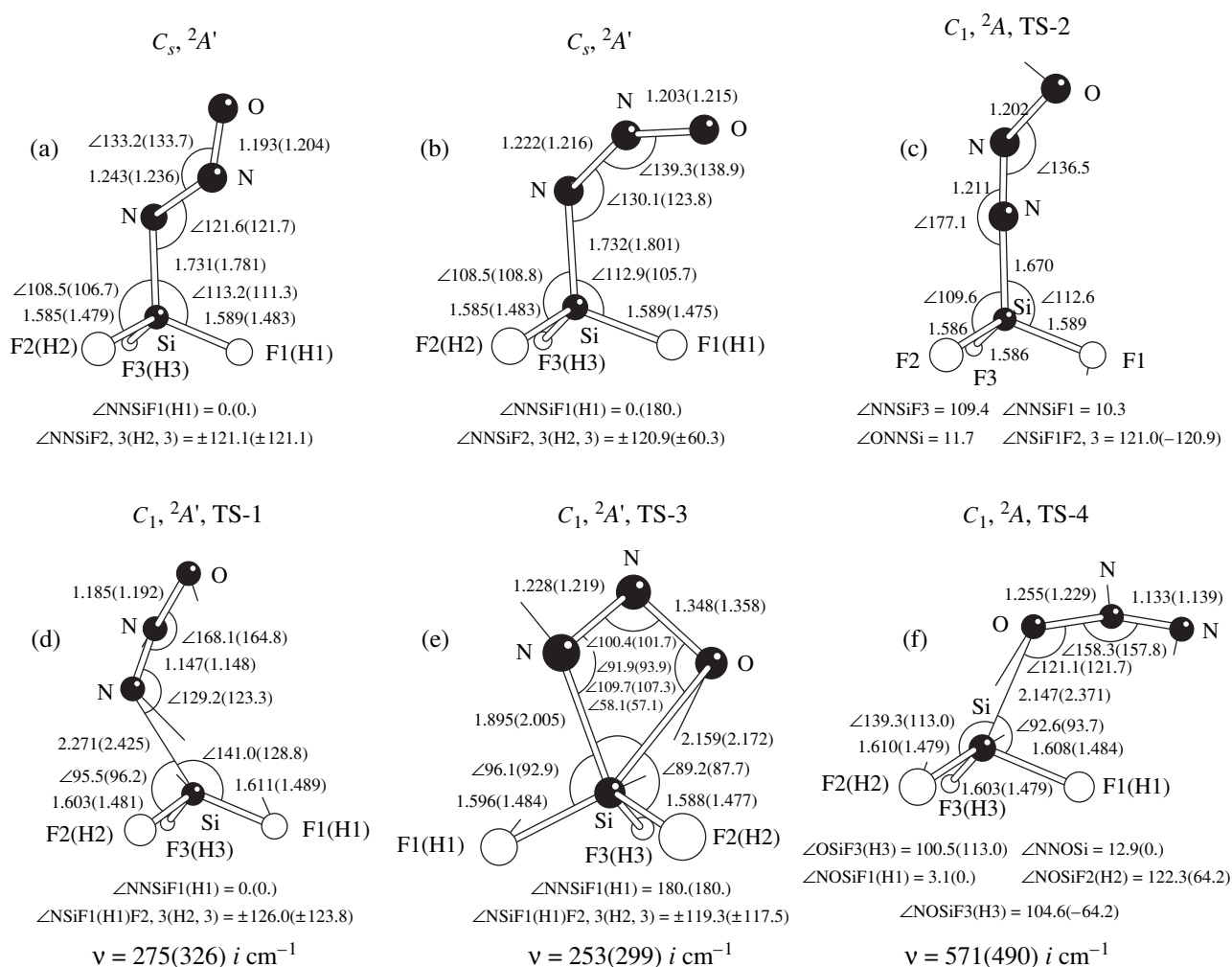


Fig. 1. Geometric characteristics of complexes and transition states (TS) for the systems $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$ and $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$ (in parentheses). For the transition states, characteristic imaginary frequencies are given and atomic shifts that take place when moving along the reaction coordinate are shown. In the structures (b) and (f), groups H_3Si and F_3Si have different orientations (see the values of the corresponding torsion angles). For the hydrogen-containing radical, transition state TS-4 has C_s symmetry. Bond lengths are in angstroms. Torsion angles are in degrees.

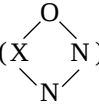
Another low frequency in the IR spectrum of the radical, 123 cm^{-1} , characterizes planar deformational vibration of the F1SiNNO fragment with the main contribution from the valence angles Si-N=N and F1-Si-N . Information on the barriers of internal deformations in the radicals will be used in the discussion of temperature dependences of radiospectroscopic characteristics.

The second minimum on the potential energy surface corresponds to the formation of the complex in the *cis*-configuration of atoms SiNNO (Fig. 1b). The vibrational spectrum for this conformer is also shown in Table 2. The *trans*-configuration is noticeably stronger: the enthalpy of its formation is lower by 6.5 kcal/mol (see Table 1). This means that, at moderate temperatures, only the *trans*-conformation of the radical is populated.

The transition state (TS) for the *trans-cis* transformation of the radical is shown in Fig. 1 (TS-2). This transition state is formed via opening the valence SiNN angle. The height of the activation barrier is 8.6 kcal/mol (DFT calculation). The activation energy of the reverse reaction is $8.6 - 6.5 = 2.1 \text{ kcal/mol}$. The value of the preexponential factor for the *trans-cis* isomerization rate constant for the $\text{F}_3\text{Si-N=N-O}^\bullet$ radical is $1.8 \times 10^{12} \text{ s}^{-1}$. For an activation barrier of 8.6 kcal/mol , the frequency of these transitions at 300 K is $1 \times 10^6 \text{ s}^{-1}$.

Another possible transition state for *trans-cis* isomerization is formed by opening the N=N-O valence angle and this process corresponds to a higher activation barrier of 23.5 kcal/mol .

Table 1. Full energies (E , atomic units), average values of the spin operator of the system ($\langle S^2 \rangle$), and the zero-point energies (ZPE , kcal/mol) of initial reactants, products, and transition states for different channels of reactions in the systems $X + N_2O$ ($X = H^\bullet, H_3C^\bullet, H_3Si^\bullet, F_2HSi^\bullet, F_3Si^\bullet, F_3Ge^\bullet$). The enthalpies of formation at 0 K ($\Delta H(DFT)$ and $\Delta H(G2)$ kcal/mol) are taken relative to the level of initial reactants*

Parameters	(X + N ₂ O)	(X...NNO) TS-1	X-NNO (<i>trans</i>)	X-NNO (<i>cis</i>)	 , TS-3	(X...ONN), TS-4	(XO + N ₂)
X = H [•]							
− E (a.u.)	185.21544	185.20755	185.26713	185.25769	185.19327	185.19655	185.31046
$\langle S^2 \rangle$	0.750	0.764	0.754	0.756	0.760	0.760	0.752
ZPE	7.0	7.45	13.2	12.7	8.9	7.5	8.8
$\Delta H(DFT)$	0.0	5.4	−26.2	−20.8	15.8	12.3	−57.9
−G2MP2	184.93247	184.91906	184.96766	184.95766	184.90471	184.90582	185.03040
$\Delta H(G2)$	0.0	8.4	−22.1	−15.8	17.4	16.7	−61.45
X = H ₃ C [•]							
− E (a.u.)	224.56704	224.54983	224.58795	224.58236	224.49177	224.53627	224.64205
$\langle S^2 \rangle$	0.754	0.772	0.755	0.756	0.780	0.776	0.753
ZPE	25.6	27.6	30.7	30.5	27.9	27.2	26.2
$\Delta H(DFT)$	0.0	12.8	−8.0	−4.7	49.5	21.0	−46.5
−G2MP2	224.17638	224.15156	224.18565	224.18065	224.09082	224.13651	224.25299
$\Delta H(G2)$	0.0	15.6	−5.8	−2.7	53.7	25.0	−48.1
X = H ₃ Si [•]							
− E (a.u.)	475.97436	475.96530	476.00417	475.99875	475.95525	475.95841	476.06685
$\langle S^2 \rangle$	0.751	0.760	0.754	0.754	0.759	0.760	0.754
ZPE	20.3	20.7	22.9	22.9	21.3	20.0	19.7
$\Delta H(DFT)$	0.0	6.1	−16.2	−12.8	13.0	9.7	−58.6
−G2MP2	475.20253	475.19060	475.23116	475.22387	475.19038	475.18362	475.30468
$\Delta H(G2)$	0.0	7.5	−18.0	−13.4	7.6	11.9	−64.1
X = F ₂ HSi [•]							
− E (a.u.)	674.63279	674.62626	674.67652	674.66865	674.62138	674.61842	674.73853
$\langle S^2 \rangle$	0.751	0.760	0.754	0.754	0.759	0.760	0.753
ZPE	15.2	15.1	16.9	16.9	15.35	15.6	14.2
$\Delta H(DFT)$	0.0	4.1	−25.7	−20.74	7.34	8.44	−67.0
−G2MP2	673.64965	673.64097	673.69255	673.68297	673.64919	673.63213	673.76761
$\Delta H(G2)$	0.0	5.45	−26.9	−20.9	0.3	11.0	−74.0
X = F ₃ Si [•]							
− E (a.u.)	773.96655	773.96068	774.01151	774.00268	773.95853	773.95257	774.07110
$\langle S^2 \rangle$	0.751	0.761	0.754	0.754	0.759	0.759	0.752
ZPE	12.2	12.1	13.4	13.4	11.85	11.45	10.8
$\Delta H(DFT)$	0.0	3.6	−27.0	−21.5	4.7	8.0	−67.0
−G2MP2	772.87984	—	—	—	—	—	772.99842
ΔH_{corr}	0.0	5.0	−28.2	−21.7	−3.7	10.6	−74.4
X = F ₃ Ge [•]							
− E (a.u.)	2561.39848	2561.38748	2561.40165	2561.39564	2561.36001	2561.38007	2561.45444
$\langle S^2 \rangle$	0.752	0.764	0.754	0.755	0.763	0.760	0.753
ZPE	10.8	10.6	11.6	11.5	10.1	9.75	9.1
$\Delta H(DFT)$	0.0	6.7	−1.2	1.6	23.5	10.5	−36.8
ΔH_{corr}	0.0	8.1	−2.4	1.4	16.5	13.1	−44.2

* Calculations at the DFT level. For the systems $H^\bullet + N_2O$, $H_3C^\bullet + N_2O$, $H_3Si^\bullet + N_2O$, and $F_2HSi^\bullet + N_2O$, the values of energies calculated at the G2MP2 level are given for 0 K [26] for the structures optimized at the DFT level. They are used to calculate the relative values of $\Delta H(G2)$.

Figure 2 (curve 2) shows the dependence of the energy of the *trans*-configuration of the $F_2HSi-N=N-O^\bullet$ radical on the angle of the internal rotation around the Si-N bond. The values of the HSiNN torsion angles equal to 180° (Z_1) and 0° (Z_2) correspond to two minima on the potential energy surface. Table 2 shows the results of the calculation of vibrational spectra for these radical conformations. A change in the structure of the coordination sphere of the silicon atom and a decrease in its local spatial symmetry results in an increase in the barrier to internal rotation around the Si-N bond in the radical, although its value remains comparatively low (0.6 kcal/mol).

Figure 1d shows the structure of the transition state corresponding to the addition of nitrous oxide to the $F_3Si^\bullet$ radical (TS-1). In the transition state with C_s symmetry, the ONNSi atoms are in the *cis*-configuration. At long distances between Si and N atoms, this configuration has a lower energy than the *trans*-configuration. After passing through the maximum and as the Si and N atoms approach each other, the difference in the full energies of *cis*- and *trans*-configurations decreases and then the latter configuration becomes energetically more favorable and an energetic barrier separates these configurations. Thus, the addition of nitrous oxide results in the formation of the *cis*-configuration, which then transforms into the more stable *trans*-configuration.

In addition to the reverse reaction (the abstraction of nitrous oxide), another possible channel for the transformation of the complex is its isomerization and decomposition resulting in the formation of the oxy radical $F_3Si-O^\bullet$ and molecular nitrogen. These products correspond to the absolute minimum on the poten-

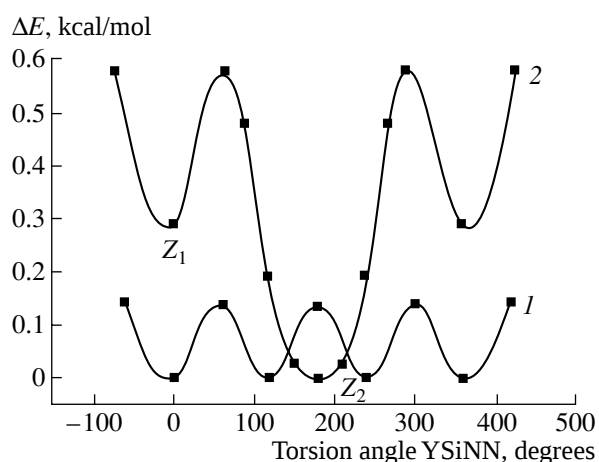


Fig. 2. Dependences of the energies of radicals $F_2YSi-N=N-O^\bullet$ (the *trans*-conformation of the SiNNO fragment) on the value of the torsion angle YSiNN for Y = F (1) and H (2).

tial energy surface of the $F_3Si^\bullet + N_2O$ system. For the H + N_2O system, such a state is $(HO^\bullet + N_2)$. Marshall *et al.* [14] showed, using quantum chemical methods, that the corresponding products can be formed by isomerization with the decomposition of the $H-N=N-O^\bullet$ radical. This reaction occurs via a cyclic four-membered transition state (the 1,3-shift of a hydrogen atom).

Figure 1e shows the cyclic transition state for isomerization with the decomposition of the $F_3Si-N=N-O^\bullet$ radical resulting in the formation of $F_3Si-O^\bullet + N_2$ (TS-3). In the transition state, the silicon atom is five-coordinated. The hydrogen atom displaces silicon and the Si-O bond is formed instead of the Si-N bond. As silicon and oxygen atoms approach each other, the N-O bond

Table 2. Calculated frequencies and their intensities (km/mol, in parentheses) in the IR spectra of the radicals $F_3Si-N=N-O^\bullet$ and $F_2HSi-N=N-O^\bullet$ *

$F_3Si-N=N-O^\bullet$ (<i>trans</i>)
30(0.2), 123(1.8), 200(8.1), 260(3.1), 265(6.0), 333(41), 375(30), 383(39), 563(90), 804(53), 928(241), 998(207), 1003(210), 1414(63), 1719(569)
$F_3Si-N=N-O^\bullet$ (<i>cis</i>)
22(0.1), 100(0.4), 212(1.5), 231(0.1), 291(11), 341(30), 366(73), 432(33), 653(51), 734(6.6), 873(278), 996(197), 1004(214), 1379(1.8), 1780(712)
$F_2HSi-N=N-O^\bullet$ (z_1)
7(1.5), 132(3.7), 179(9.8), 297(20), 313(3.7), 411(50), 560(122), 831(27), 842(8.9), 843(30), 930(308), 970(250), 1402(72), 1706(606), 2376(74)
$F_2HSi-N=N-O^\bullet$ (z_2)
36(0), 163(6.2), 207(10), 270(14), 317(2.3), 387(39), 558(62), 826(84), 836(14), 860(88), 918(337), 980(240), 1401(40), 1709(574), 2337(79)

* Structures z_1 and z_2 correspond to *trans*-conformations ($\angle SiNNO = 180^\circ$) of the $F_2HSi-N=N-O^\bullet$ radical (see Fig. 2).

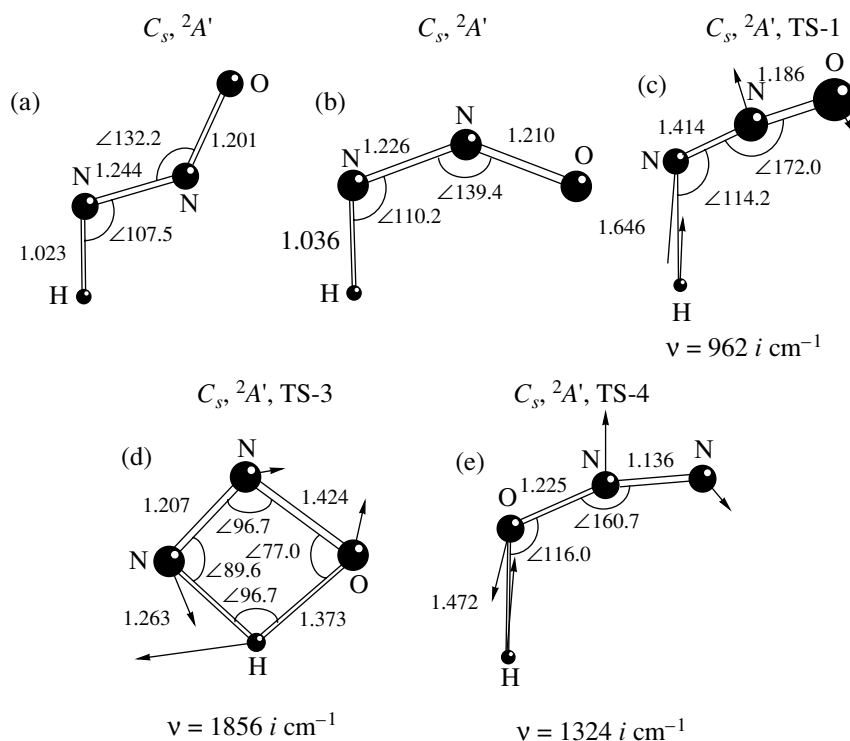


Fig. 3. Geometric characteristics of complexes and transition states (TS) for the system $\text{H} + \text{N}_2\text{O}$. Bond lengths are in angstroms. Torsion angles are in degrees. For the transition states, characteristic imaginary frequencies are given and atomic shifts that take place when moving along the reaction coordinate are shown.

becomes longer and cleaves. The oxy radical and a nitrogen molecule are the products of this reaction. Note that this transition state is possible if the $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical is in the *cis*-configuration. According to the calculations, the energy of this transition state is lower than the energy of the transition state corresponding to the abstraction of nitrous oxide molecule (Table 1).

Thus, one of the possible channels to the final products of the reaction of silyl-type radicals with nitrous oxide (oxy radical and molecular nitrogen) is the formation of a metastable complex and its further isomerization and decomposition.

The second channel for the reaction exists that leads to the same products. This is the direct abstraction of an oxygen atom from N_2O by a silyl radical. Figure 1f shows the structure of the transition state (TS-4) corresponding to this channel. According to the calculations (see Table 1), this channel is characterized by a high activation energy.

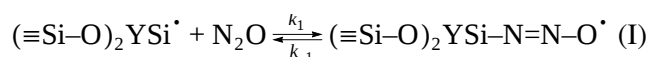
The cited structures and processes are important for other systems studied here as well ($\text{X}^\bullet + \text{N}_2\text{O}$, where $\text{X} = \text{H}, \text{H}_3\text{C}^\bullet, \text{H}_3\text{Si}^\bullet, \text{F}_2\text{HSi}^\bullet$, and $\text{F}_3\text{Ge}^\bullet$). Their spatial structures are shown in Figs. 1, 3–5, and the calculated energies of the respective state are presented in Table 1. System $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$ served as a model for the experi-

mentally studied oxidation of germyl radicals ($(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$) by nitrous oxide [10, 11] (see Section 7). The $\text{H} + \text{N}_2\text{O}$ system was calculated earlier [14, 19, 20] using other quantum chemical schemes. We reproduce them to compare with the results obtained by other methods used in this work. The consideration of the hydrocarbon radical ($\text{H}_3\text{C}^\bullet + \text{N}_2\text{O}$) allowed us to compare the reaction of nitrous oxide with different free radicals: $\text{H}^\bullet, \text{H}_3\text{C}^\bullet, \text{H}_3\text{Si}^\bullet, \text{F}_2\text{HSi}^\bullet, \text{F}_3\text{Si}^\bullet$, and $\text{F}_3\text{Ge}^\bullet$. The discussion of the results obtained in this work and their comparison with available experimental data are given below.

2. SPECTRAL CHARACTERISTICS OF THE COMPLEX OF N_2O WITH THE $\equiv\text{Si}^\bullet$ RADICALS

2.1. ESR Measurements

ESR spectra of paramagnetic centers were recorded using the ESR-20 spectrometer working in the X-range. Figure 6 shows the ESR spectrum of the radical $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ which is the product of the reaction



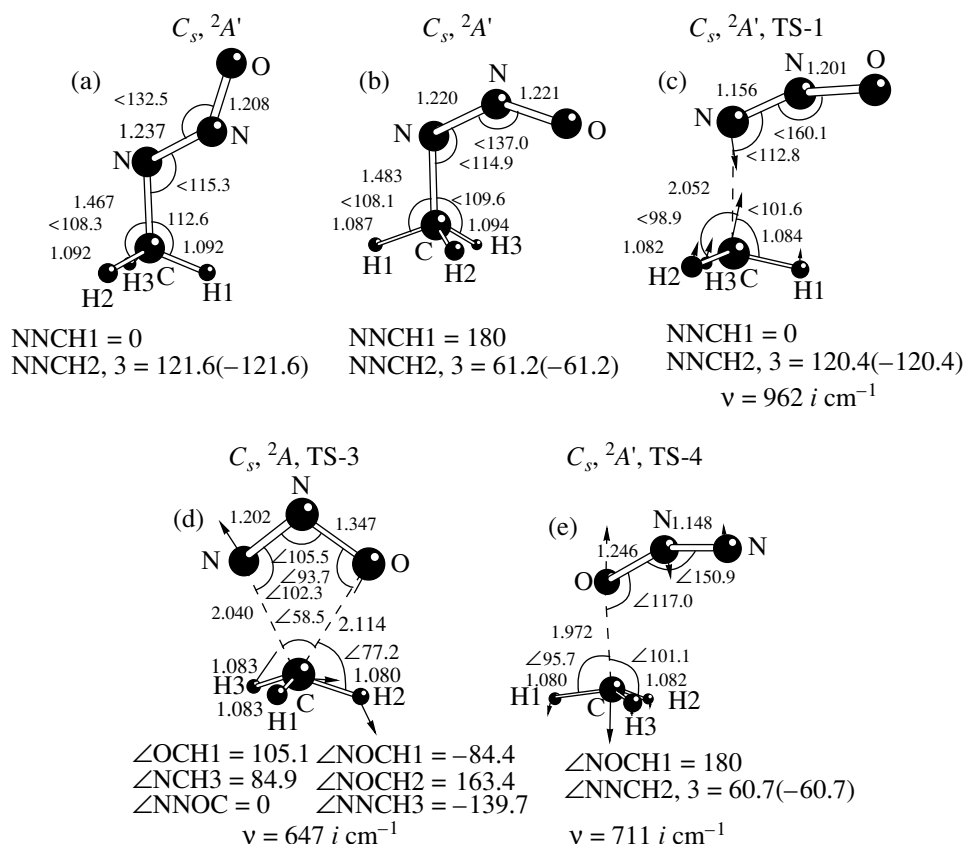


Fig. 4. Geometric characteristics of complexes and transition states (TS) for the system $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O}$. Bond lengths are in angstroms. Torsion angles are in degrees. For the transition states, characteristic imaginary frequencies are given and atomic shifts that take place when moving along the reaction coordinate are shown.

when $\text{Y} = (\equiv\text{Si}-\text{O})$ (radical **I**). At 77 K, the spectrum has three components of the hyperfine structure (hfs) with an intensity ratio close to 1 : 1 : 1 and a distance between them of ~ 36.5 G (measured between the intersection points of hfs components with the zero line). The apparent hfs of the ESR spectrum is due to the interaction of an unpaired electron with one ^{14}N nucleus ($I = 1$).

When registering the signal at 300 K, it preserves the form of a triplet with the same ratio of intensities of different components. But their form reversibly changes (Fig. 6). An increase in temperature to 300 K is accompanied by broadening the hfs components of the ESR spectrum, which is especially pronounced at the wings of the spectrum. The broadening of separate hfs components agrees with the fact that their amplitude decreases more rapidly with an increase in temperature than it follows from the Curie law (twofold difference when the temperature is changed from 77 to 300 K).

Figures 7 and 8 show the ESR spectra of radicals $(\equiv\text{SiO})_2(\text{HO})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (**II**) and $(\equiv\text{SiO})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (**III**), which are the products of N_2O addition to other silyl radicals $(\equiv\text{SiO})_2\text{HSi}^\bullet-\text{OH}$ and $(\equiv\text{SiO})_2\text{Si}^\bullet-\text{H}$. The form of ESR spectra of these com-

plexes also reversibly depends on the registration temperature (77 and 300 K). However, the nature of these changes differs from those found for the **I** radical. These differences are not associated with the presence of H(D) atoms involved in the coordination sphere of the silicon atom. The replacement of H by D in radicals **II** and **III** virtually does not affect the form of their ESR spectra. Asymmetry of ESR spectra of these complexes, which is noticeable even at 300 K increases with a decrease in the sample temperature to 77 K. In this case the hyperfine structure is clearly seen, which is due to the interaction of an unpaired electron with the second ^{14}N atom of the radical.

Figure 8 (spectrum 2) presents the simulated ESR spectrum of the radical characterized by the anisotropic g -tensor with the main values $g_1 = 2.004$, $g_2 = 2.002$, and $g_3 = 1.996$ and the tensor of the hyperfine interaction of an unpaired electron with two nitrogen nuclei. These tensors have the main values $a_1(\text{N}(1)) = 35.5$ G, $a_2(\text{N}(1)) = 41.1$ G, $a_3(\text{N}(1)) = 34.0$ G, $|a_1(\text{N}(2))| = 3.5$ G, $|a_2(\text{N}(2))| = 4.6$ G, and $|a_3(\text{N}(2))| = 4.8$ G (the choice of the positive signs of hyperfine interaction constants of an unpaired electron with the N(1) nucleus is based on the results of quantum chemical calculations, see below). The spectrum is calculated for these parameters

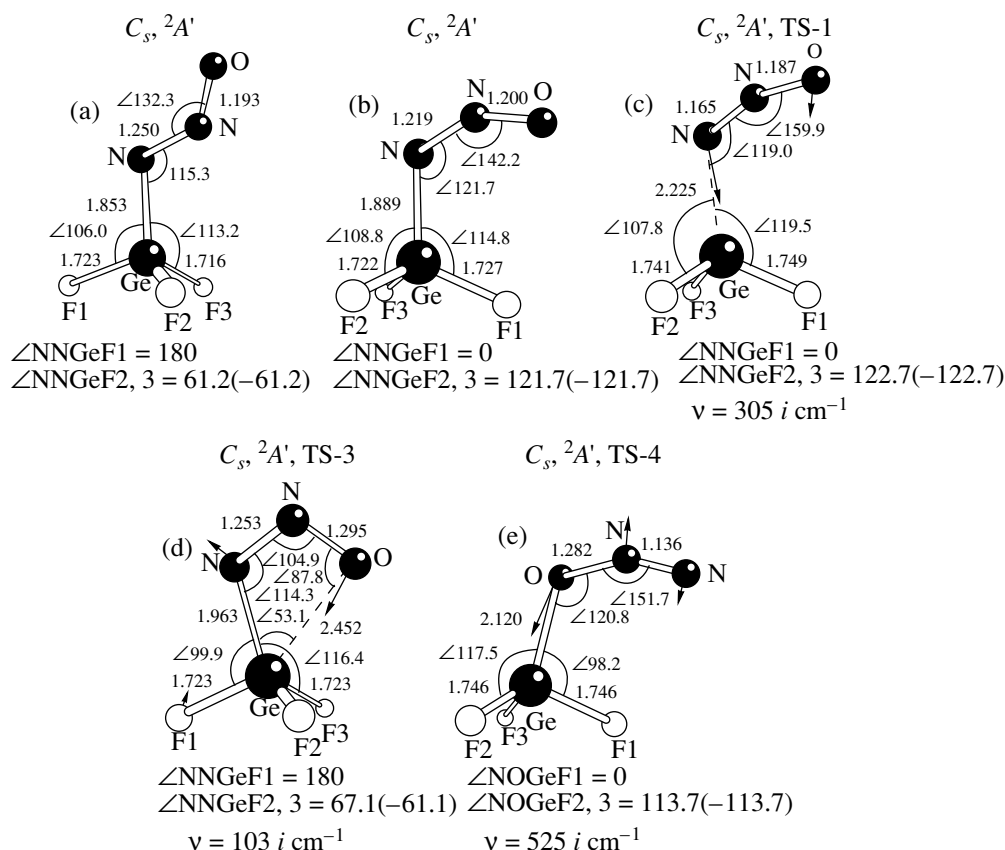


Fig. 5. Geometric characteristics of complexes and transition states (TS) for the system $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$. Bond lengths are in angstroms. Torsion angles are in degrees. For the transition states, characteristic imaginary frequencies are given and atomic shifts that take place when moving along the reaction coordinate are shown.

of the spin-Hamiltonian using the first-order perturbation theory assuming the coincidence of the main axes of all tensors and the Lorenz form of the individual component. The simulation reflects the main features of the form of the ESR signal for radical **III**. Thus, for this

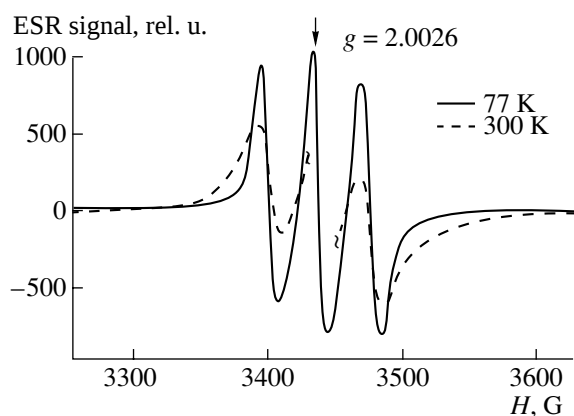


Fig. 6. ESR spectra of the $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical (the central component of the spectrum at 300 K is distorted by the superposition of the admixed signal and is not shown).

radical, $g_{\text{iso}} = 1/3 (g_1 + g_2 + g_3) = 2.001$ and $a_{\text{iso}}(\text{N}(1)) = 1/3(a_1 + a_2 + a_3) = 36.9$ G. The estimate of the value of the isotropic constant of hyperfine interaction with the N(2) nucleus is complicated by the fact that the signs of the main components of the corresponding tensor are unknown. Since the resolved hyperfine structure associated with the second nitrogen atom cannot be observed at room temperature by the registration of the ESR signal from the complexes and taking into account the width of individual components of the ESR spectrum, we conclude that $|a_{\text{iso}}(\text{N}(2))| \leq 4$ G.

Figure 8 (spectrum 3, dashed line) shows the ESR spectrum fragment for radical **III** on the silica surface enriched with the ^{29}Si isotope ($I = 1/2$, the concentration is 95%). The spectrum clearly shows the duplet splitting of each component of the spectrum with a hyperfine interaction constant of 10.5 ± 0.5 G. An analogous pattern was observed for radicals **I** and **II**. Thus, a small portion of spin density in these radicals is localized on the silicon atom.

Table 3 shows the calculated radiospectroscopic characteristics of the radicals $\text{F}_3\text{Si}-\text{N}(2)=\text{N}(1)-\text{O}^\bullet$ and $\text{F}_2\text{HSi}-\text{N}(2)=\text{N}(1)-\text{O}^\bullet$ (the SiNNO fragment in the *trans*-configuration). These radicals are molecular

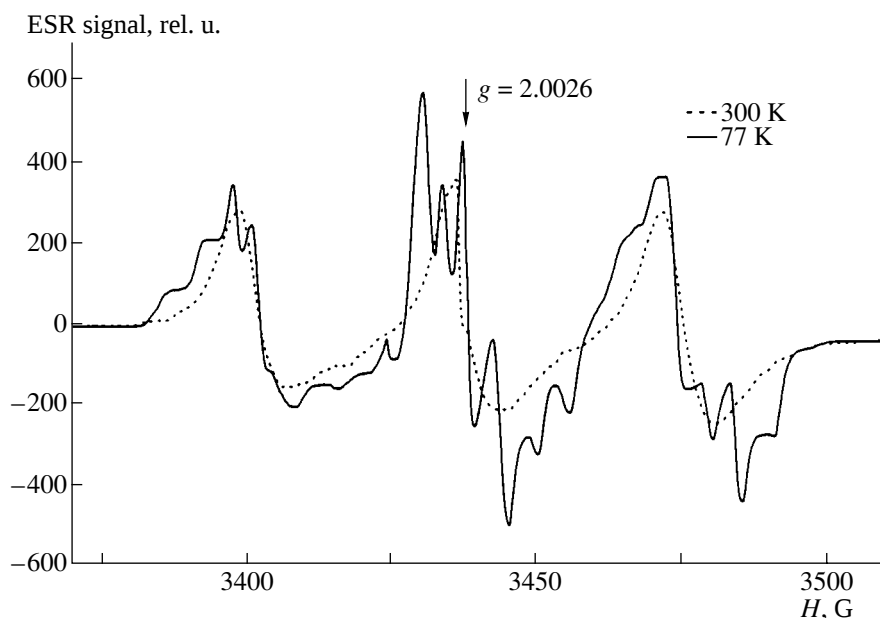


Fig. 7. ESR spectra of the $(\equiv\text{Si}-\text{O})_2(\text{HO})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical.

models of the surface sites $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ and $(\equiv\text{Si}-\text{O})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$.

Data from Table 3 shows that the calculated and experimental values of the isotropic constants of the hyperfine interaction of an unpaired electron with ^{29}Si , $^{14}\text{N}(1)$, and $^{14}\text{N}(2)$ nuclei for the main (*trans*) configuration of the $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical are in acceptable agreement. The spin density in the complex is distributed between oxygen and nitrogen atoms (Table 3). On the terminal oxygen atom, the unpaired electron occupies the $2p$ atomic orbital (AO). On the nitrogen atom, it occupies sp^n AO, and the density maxima of all orbitals are in the symmetry plane of the radical (C_s symmetry, $^2A'$ state). Thus, the formula $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ in which the three valence is localized on the oxygen atom is just conventional.

Table 3 also shows the results of the calculation of radiospectroscopic characteristics for the *cis* form of the radical $\text{F}_3\text{Si}-\text{N}(2)=\text{N}(1)-\text{O}^\bullet$ (Fig. 1b). Although the distributions of spin density for *cis* and *trans* isomers of the radical are similar, substantial differences in the values of the hyperfine interaction constants of an unpaired electron with ^{29}Si , $^{14}\text{N}(2)$, and $^{14}\text{N}(1)$ nuclei are notable for these two radical isomers.

As calculations show for the main configuration of the $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical, the constant of hyperfine interaction with nitrogen nuclei should have a greater anisotropic component (see Table 3). However, even at the temperature of ESR signal registration (77 K) of radicals **II** and **III**, the apparent anisotropy of hyperfine interaction constants is noticeably lower. We can judge

this from the value of the constant of hyperfine interaction with the $\text{N}(1)$ nuclei: the experimental value of its anisotropy is lower than 6 G, although the calculated value is almost 22 G. This points to the fact that, even at 77 K, the intramolecular mobility in these radicals results in the partial averaging of anisotropic interactions.

We expect that for a radical with a similar structure, as well as for other oxy and peroxy radicals, one of the main components of its g -tensor will be directed along the $\text{N}-\text{O}$ bond or slightly inclined. For this component of the g -tensor, we expect the maximal shift $\Delta g = g - g_e$ relative to the value characteristic of the free electron ($g_e = 2.0023$). This shift is determined by admixing electronically excited states with $^2A''$ symmetry to the main state at the expense of the spin-orbital interaction. In these electronically excited states, the maximum of spin density is perpendicular to the plane of radical symmetry. The value $\Delta g \sim -\lambda/(\Delta E)^{-1}$ (where ΔE is the difference between the energies of molecular orbitals (MO) occupied by an unpaired electron in the excited and main states and λ is the constant of spin-orbital interaction [29]). The sign of ΔE is positive for the electronically excited states. The calculation of the vertical electronically excited state $^2A''$ of the $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical with the lowest energy showed that this state corresponds to the excitement of an unpaired electron and its transfer to a higher MO. That is the value of ΔE is positive. Therefore, we conclude that the components $g_3 = 1.996$ (1.995) and $a_3(\text{N}(1)) = 34$ (34.5) G are directed along the $\text{N}-\text{O}$ bond.

Because the directions of the $\text{N}-\text{O}$ and $\text{Si}-\text{N}$ bonds for the *cis*-conformation of the radicals differ only

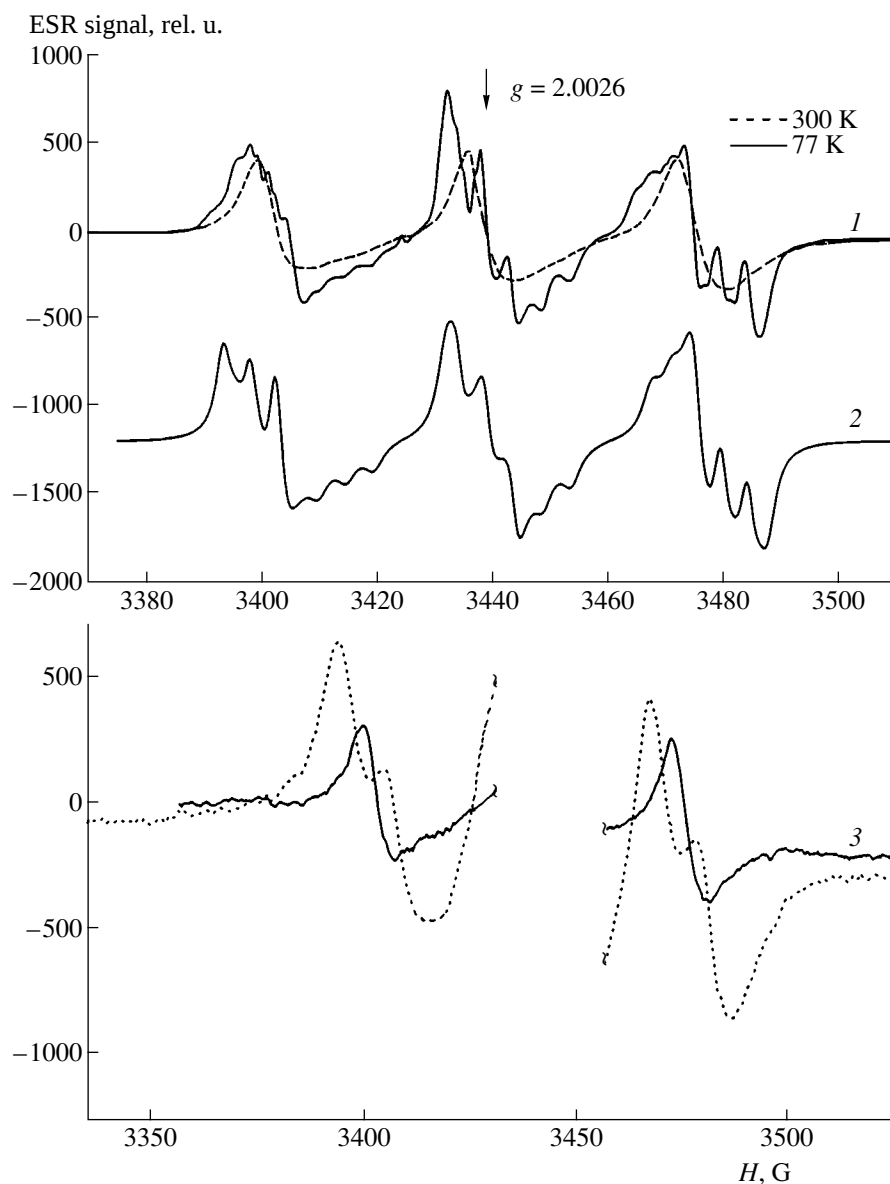


Fig. 8. ESR spectra of radicals (1) $(\equiv\text{Si}-\text{O})_2(\text{H})^{28}\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$; (2) $\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ (calculated); (3) $(\equiv\text{Si}-\text{O})_2(\text{H})^{28}\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (solid line) and $(\equiv\text{Si}-\text{O})_2(\text{H})^{29}\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (dashed line, registration at 300 K).

slightly (according to the calculation, the angle between them is $\sim 11^\circ$), defreezing the internal rotation around the Si-N bond should not result in considerable changes in the values of g_3 and $a_3(\text{N}(1))$. Indeed, in agreement with experimental data, this part of ESR spectra of the **II** and **III** radicals (see Figs. 7 and 8) is less susceptible to the averaging effect of intramolecular deformations at 300 K. If we consider that, at 300 K, the g - and a -tensors have axial symmetry, then $g_{\parallel} \cong 1.996$ (1.995), $g_{\perp} \cong 2.0026$ (2.0025), $a_{\parallel} \cong 34$ (34.2) G, and $a_{\perp} \cong 36.2$ (36.5) G.

The ESR spectra of radicals **I**, **II**, and **III**, which have close chemical structures, registered at the same temperature have noticeably different shapes (see Figs. 6-8).

This fact points to the high rotational mobility of the **I** radical. A similar radical was also observed for the radicals $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}-\dot{\text{C}}\text{H}_2$ and $(\equiv\text{Si}-\text{O})_2(\text{HO})\text{Si}-\text{O}-\dot{\text{C}}\text{H}_2$ [30]. It was especially pronounced when the ESR spectra were recorded at 77 K. In this case too, the appearance of the hydroxyl group as a substituent of the silicon atom resulted in a decrease in the rotational mobility of the free-radical fragment $-\text{O}-\text{CH}_2$. According to the calculation, a change in the structure of the coordination sphere of the silicon atom (the replacement of $-\text{F}$ for $-\text{H}(\text{D})$) is accompanied by an increase in the height of the barrier to the rotation of the free-radical fragment around the Si-N bond (Fig. 2).

With an increase in the registration temperature from 77 to 300 K, the width of the hfs components of the ESR spectrum for radical **I** increases (Fig. 6). With an increase in temperature, the lines in the ESR spectrum are usually narrowed due to averaging anisotropic interactions with an increase in amplitudes and frequencies as the temperature is increased. An increase in the width of the band points to a shorter duration of spin relaxation of an unpaired electron with an increase in temperature. Proceeding from the value of hfs component broadening of radical **I** (~10 G), this time is 10^{-7} – 10^{-8} s at 300 K.

For the radical fragments grafted to solid surface and deprived of the translational degrees of freedom when the distance between them is several tens of angstroms, relaxation effects are controlled by their intramolecular mobility. Various processes are known that result in the broadening of spectral lines. The $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radicals (see Section 2) may have *trans*- and *cis*-conformations, which have different constants of the hyperfine interaction of an unpaired electron with nitrogen nuclei (see table 3). Transitions between these conformations may result in line broadening in the spectrum. However, their populations at room temperature differ by more than 1000 times (see Section 2) and the exchange effect would be insignificant [31].

Line broadening due to shortening the time needed for spin–lattice relaxation (T_1) relates to the time of the correlation (τ_c) of intramolecular deformations in the radical by the expression [31]

$$T_1^{-1} = (8\pi^2/15)(H^2)h^{-2}\tau_c(1 + 4\pi^2\nu_0^2\tau_c^2)^{-1},$$

where h is the Planck constant, ν_0 is the Zeeman frequency of electron spin precession in an external magnetic field; and H^2 is the average value of the square of fluctuating magnetic field affecting the electron spin. This field can be due to the anisotropic components of the g -tensor and the tensors of hyperfine interaction of an unpaired electron with magnetic momentums of radical nuclei or due to rotational interaction [32]. The maximal line width corresponds to the condition $2\pi\nu_0\tau_c = 1$ (further, with an increase in τ_c this value decreases according to the formula cited above). Assuming that line broadening is equal to 10 G, we obtain that, at $2\pi\nu_0\tau_c = 1$, the value of (H^2) is $1.6 \times 10^5 \text{ G}^2$. That is, the amplitude of fluctuating magnetic field is several hundreds of gauss. A field with such value can hardly be due to the anisotropic components of the g -tensor and the tensors of hyperfine interaction of an unpaired electron with the magnetic momentums of radical nuclei (Figs. 6–8, Table 3). The spin–rotation relaxation can be due to the motion of the $-\text{N}=\text{N}-\text{O}$ fragment around the Si–N bond, which is a slightly hindered monoaxial rotation in the $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radicals (see Section 1). The difference in line broadening in the ESR spectra at 300 K can be associated with the difference in rotational activities of radical **I** and radicals **II**

and **III** (for radicals **II** and **III**, line broadening is less pronounced). However, the estimates of the contribution of this mechanism to the broadening of spectral line have not been made. Thus, the reason for this apparent effect is yet unclear.

2.2. IR Spectroscopic Measurements

IR spectroscopic measurements were carried out using pressed samples of high-dispersity aerosil (semi-transparent films, 50–100- μm thick films [33]) placed in a special cell with silicon windows. We were able to record IR spectra with wave numbers greater than $\geq 1300 \text{ cm}^{-1}$ when the silica glass transparency was 850 – 950 cm^{-1} . IR spectra were recorded at room temperature using a Digilab Fourier-transform spectrometer with 256 scans and 4-cm^{-1} resolution.

Table 3. Calculated distributions of spin densities of isotropic (a_{iso}) and anisotropic (b_1 , b_2 , and b_3) constants of the hyperfine interaction of electron with magnetic isotopes of nuclei in the radicals $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ and $\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ *

Isotopes	Atomic spin density	Hyperfine interaction constants, G			
		a_{iso}	b_1	b_2	b_3
$\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (<i>trans</i>)					
^{17}O	0.35	−12.9	23.3	21.0	44.3
^{14}N	0.43	34.0	−7.8	−7.1	14.8
^{14}N	0.21	−3.1	−6.1	−4.6	10.8
^{29}Si	0.02	−9.7	1.2	1.2	−2.4
$\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (<i>cis</i>)					
^{17}O	0.35	−14.9	22.8	20.7	−43.5
^{14}N	0.45	50.8	−8.3	−7.2	15.5
^{14}N	0.10	41.8	−3.2	−1.5	4.8
^{29}Si	0.08	−66.2	3.5	3.4	−6.8
$\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ (z_1)					
^{17}O	0.33	−13.2	−	−	−
^{14}N	0.43	33.4	−	−	−
^{14}N	0.22	−2.7	−	−	−
^{29}Si	0.02	−14.9	−	−	−
^1H	0.00	−1.0	−	−	−
$\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ (z_2)					
^{17}O	0.34	−12.8	−	−	−
^{14}N	0.42	31.7	−	−	−
^{14}N	0.22	−2.9	−	−	−
^{29}Si	0.02	−11.9	−	−	−
^1H	0.01	0.6	−	−	−

* Structures z_1 and z_2 correspond to two *trans*-conformations ($\angle\text{SiNNO} = 180^\circ$) of the $\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ radical (see Fig. 2).

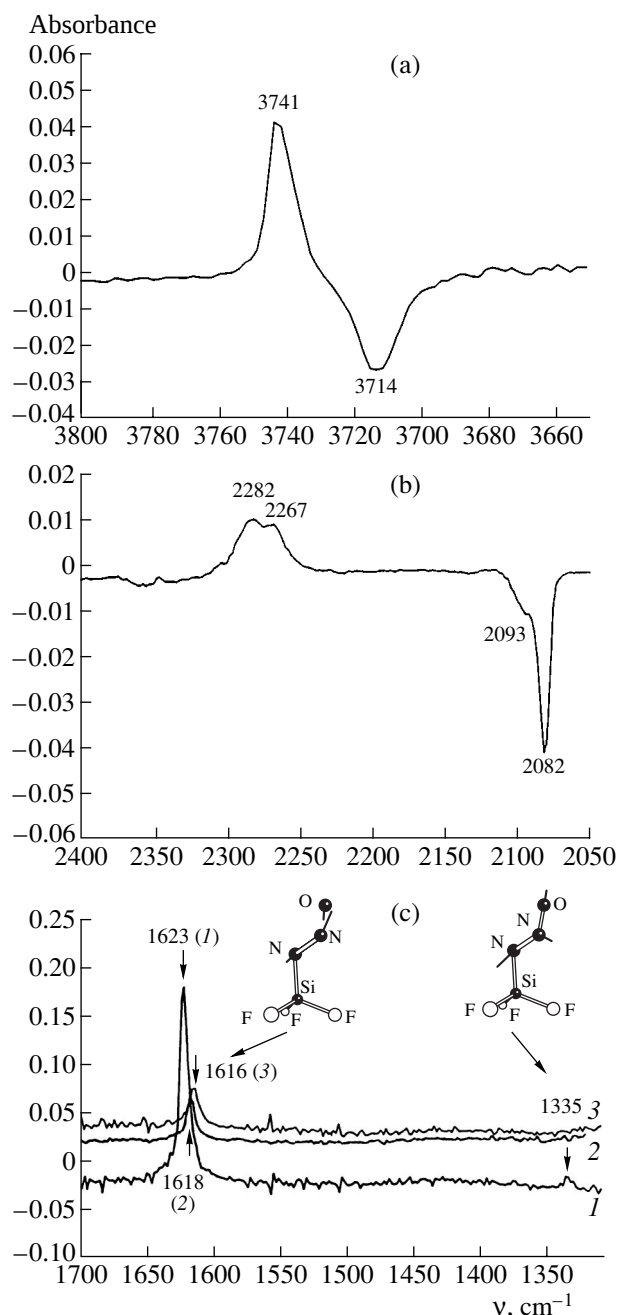


Fig. 9. IR spectra of the products of $\equiv \text{Si}^\bullet$ reactions with N_2O molecules (at 300 K): (a) changes in the IR spectrum during the reaction $(\equiv \text{Si}-\text{O})_2(\text{HO})\text{Si}^\bullet \rightarrow (\equiv \text{Si}-\text{O})_2(\text{HO})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (a fragment of the difference spectrum); (b) changes in the IR spectrum during the reaction $(\equiv \text{Si}-\text{O})_2(\text{H})\text{Si}^\bullet \rightarrow (\equiv \text{Si}-\text{O})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (a fragment of the difference spectrum); and (c) fragments of IR spectra for the radicals (1) $(\equiv \text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$, (2) $(\equiv \text{Si}-\text{O})_2(\text{HO})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$, and (3) $(\equiv \text{Si}-\text{O})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$. Calculated form of two normal vibrations of the radical $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ are shown.

Figure 9 shows changes on the IR spectra of the samples upon the addition of nitrous oxide molecules to the radicals $(\equiv \text{Si}-\text{O})_3\text{Si}^\bullet$, $(\equiv \text{Si}-\text{O})_2\text{Si}^\bullet-\text{OH}$, and $(\equiv \text{Si}-\text{O})_2\text{Si}^\bullet-\text{H}$. The formation of $\equiv \text{Si}-\text{O})_2(\text{HO})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (**II**) is accompanied by a shift of the band of the O-H group stretch in the radical $(\equiv \text{Si}-\text{O})_2\text{Si}^\bullet-\text{OH}$ from 3714 [22] to 3741 cm^{-1} (Fig. 9a). Recall that the absorption band of isolated $(\equiv \text{Si}-\text{O})_3\text{Si}-\text{OH}$ groups on the silica surface is at 3747 cm^{-1} .

An absorption band in the range 2080–2090 cm^{-1} (Fig. 9b) refers to the Si-H group stretch in the $(\equiv \text{Si}-\text{O})_2\text{Si}^\bullet-\text{H}$ radical [22]. As a result of radical $(\equiv \text{Si}-\text{O})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (**III**) formation, this band shifts to 2270–2280 cm^{-1} . A short-wave shift of the bands of O-H and Si-H groups upon nitrous oxide addition is supported by the results of quantum-chemical calculation. Thus, in the $\text{F}_2\text{Si}^\bullet-\text{H}$ radical, the stretching frequency of the Si-H group is 2132 cm^{-1} , whereas in the $\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ radical this group is characterized by a band at 2376 and 2337 cm^{-1} (depending on the conformation, see Table 2).

The formation of radicals **I**, **II**, and **III** is accompanied by the appearance of two new IR bands (Fig. 9b). One of them near 1620 cm^{-1} is very intensive. Its maximum shifts from 1623 for radical **I** to 1616 cm^{-1} for radical **III**. The second, much less intense band is near 1335 cm^{-1} . We managed to register it only for the radical **I** (the concentration of these radicals in the sample was higher).

Table 2 shows the results of the calculation of vibrational spectra of the radicals $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ and $\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$, which are molecular models of the paramagnetic centers $(\equiv \text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ and $(\equiv \text{Si}-\text{O})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$. Frequencies 1719 (1708) and 1414 (1406) cm^{-1} (frequencies for $\text{F}_2\text{HSi}-\text{N}=\text{N}-\text{O}^\bullet$ are given in parentheses) refer to the stretching vibrations of the $-\text{N}=\text{N}-\text{O}$ fragment. The form of the corresponding normal vibrations is shown in Fig. 9c. The band near 1700 cm^{-1} has very high intensity. The intensity of the second band is almost an order of magnitude lower according to the calculation.

Calculations usually overestimate the frequencies of vibration. This is due to the neglect of vibration anharmonism and with inaccuracy in the calculation of the molecule force field. An empirical correction of calculated frequencies was made using the ratio of measured and calculated frequencies of similar vibrations in the $\text{N}=\text{N}=\text{O}$ molecule as a scaling factor. The frequencies of stretching vibrations in this molecule are 2224 and 1285 cm^{-1} [34], whereas the respective frequencies calculated at the DFT level are 2335 and 1338 cm^{-1} . After correction, the frequencies for the radicals $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$

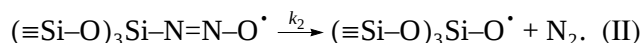
(F₂HSi-N=N-O[•]) are 1719 → 1719(2224/2335) = 1637 cm⁻¹ (1708 → 1627 cm⁻¹), and 1414 → 1414(1285/1338) = 1358 cm⁻¹ (1406 → 1350 cm⁻¹). These values are in acceptable agreement with experimental data and reflect a decrease in the frequency of the high-frequency band when switching from (≡Si-O)₃Si-N=N-O[•] to (≡Si-O)₂(H)Si-N=N-O[•]. Thus, the results of IR study support the proposed structure of the product of nitrous oxide addition to the ≡Si[•] radicals.

2.3. Optical Characteristics

of Radicals (≡Si-O)₃Si-O[•] and (≡Si-O)₃Si-N=N-O[•]

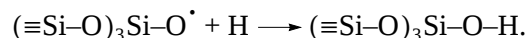
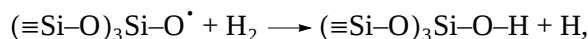
The spectrum of optical absorption of the radicals (≡Si-O)₃Si-N=N-O[•] was recorded by Bobyshev and Radtsig [5, 6] and at that time we assumed that the structure of this radical is (≡Si-O)₃Si-O-N=N[•]. Measurements were carried out using high-dispersity silica powder in the regime of the registration of light diffuse scattering. In this work, the spectra were registered at 300 K using filmed (~50-μm thick) samples of pressed silica and a Specord-40 spectrometer working in the regime of transmittance.

The (≡Si-O)₃Si-N=N-O[•] radicals were formed by reaction (I). When the sample containing these centers are heated at 400 K, the reaction of their decay



occurs. As a result of these transformations, one center disappears and another one is formed. It is possible to obtain the spectrum of optical absorption of the radical under study if the absorption spectrum of the second center is known or if the second center has no bands comparable in the intensity in the range that is of interest to us. However, all radicals (≡Si-O)₃Si[•], (≡Si-O)₃Si-O[•], and (≡Si-O)₃Si-N=N-O[•] have bands in the UV region [5, 22]. Therefore, we first obtained the spectrum of optical absorption of the (≡Si-O)₃Si-O[•] radicals. With this goal, we prepared the silica sample with oxy radicals stabilized on its surface and no other chemically active paramagnetic or diamagnetic centers (for details of the procedure, see [35]). The amount of radicals in the sample was $(7 \pm 0.5) \times 10^{15}$ (estimated from the volume of N₂ formed by reaction (II)). Then, the sample was treated by molecular hydrogen at room temperature. The number of chemisorbed H₂ molecules was $N(\text{H}_2) = (3 \pm 0.2) \times 10^{15}$ molecules per sample, that is, half the amount of oxy radicals in the sample. Consequently, the main channels for

hydrogen consumption under these conditions are two reactions of oxy radical decay [36]:



The ≡Si-O-H groups formed in these two reactions have no optical absorption bands in the studied range as controlled by IR spectroscopy using the band at 3747 cm⁻¹. Therefore, the difference spectrum of the sample before and after treatment with hydrogen is the spectrum of the optical absorption of oxy radicals (Fig. 10a).

The maximum of the optical absorption bands of the (≡Si-O)₃Si-O[•] radical are near 4.9 and 2.0 eV. The concentrations of oxy radicals in the sample are known from volumetric measurements (see above). The extinction coefficients determined from these data are $\epsilon_{\text{max}}(2.0 \text{ eV}) = (2.3 \pm 0.2) \times 10^{-20} \text{ cm}^2/\text{molecule}$ and $\epsilon_{\text{max}}(4.9 \text{ eV}) = (1.8 \pm 0.2) \times 10^{-18} \text{ cm}^2/\text{molecule}$. The strengths of the oscillators of transitions were calculated using the formula $f = 4.32 \times 10^{-9} F \int \epsilon(\omega) d\omega$, where ϵ is expressed in l mol⁻¹cm⁻¹, and ω is expressed in cm⁻¹ [37]. They are $f(2.0 \text{ eV}) = (7.4 \pm 2) \times 10^{-5}$ and $f(4.9 \text{ eV}) = (5.2 \pm 1) \times 10^{-2}$ (factor F that characterizes the effect of medium was set equal to unity).

The values obtained in this work differ from those reported in [5]. The reason for this difference is that the spectrum in [5] was recorded in the regime of the registration of light diffuse scattering. In the long-wave region, where light scattering by high-dispersity silica powder is less pronounced, the optical length of the light ray increases and this results in an apparent increase in the intensity of absorption bands in this region. To correct the obtained spectra, one can use the Kubelka-Munk theory [38], which takes into account these effects, but we did not do that in [5].

The (≡Si-O)₃Si-O[•] radical refers to the fundamental proper defects of quartz and data on its optical properties are of self-interest. The results obtained generally agree with the estimated strengths of oscillators for the optical transitions of the centers of this type stabilized in the bulk of quartz: $f(2.0 \text{ eV}) = 1.5 \times 10^{-4}$ and $f(4.8 \text{ eV}) = 5 \times 10^{-2}$ [39]. Note that the maximum of the short-wave absorption band of bulk radicals is at 4.7–4.8 eV. This is another example of the short-wave shift of the optical absorption bands of quartz surface centers relative to the bands of bulk centers [22, 23].

The spectrum of optical absorption of the (≡Si-O)₃Si-N=N-O[•] radical (Fig. 10b) was obtained by summing the difference spectrum corresponding to radical transformation by reaction (II) and the spectrum of oxy radicals. It consists of three bands with maxima at 3.25, 5.2, and >6 eV. The first two of them have com-

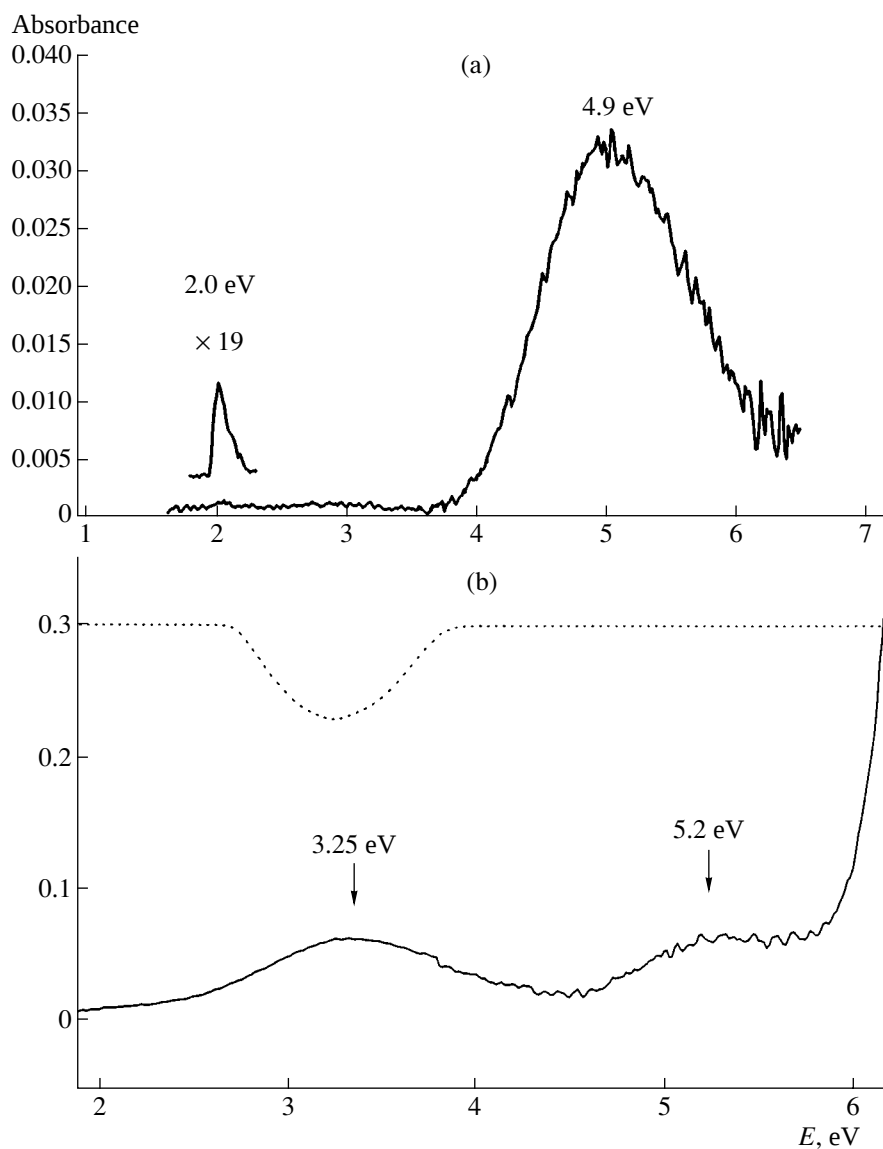


Fig. 10. Optical absorption spectra of the radicals (a) $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}^\bullet$ and (b) $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ (at 300 K). The spectrum of SF-1 filter transmittance is shown with a dashed line in part b.

parable intensities, and the intensity of the third band is much higher. The concentration of paramagnetic centers in the sample was determined by the volumetric method by measuring the amount of chemisorbed nitrous oxide molecules in reaction (I) or by measuring the amount of N_2 molecules formed by reaction (II). This allowed us to measure the coefficients of extinction of absorption bands. For the band at 3.2 eV, it was $(0.8 \pm 0.2) \times 10^{-18} \text{ cm}^2/\text{molecule}$. The estimated oscillator strength of this optical transition was $(2.0 \pm 0.2) \times 10^{-2}$. These values differ from those reported in [5] for the same reasons as in the case of oxy radicals (see above). The corresponding characteristics of the optical absorption bands with a maximum near 5.3 eV are 1.5–2 times lower. For the short-wave band with the

maximum at energies higher than 6 eV, $\epsilon(203 \text{ nm}) = (2.65 \pm 0.6) \times 10^{-18} \text{ cm}^2/\text{molecule}$.

3. KINETICS OF $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ RADICAL FORMATION AND DECOMPOSITION

Figure 11 shows kinetic data for $(\equiv\text{Si}-\text{O})_2\text{YSi}-\text{N}=\text{N}-\text{O}^\bullet$ radical formation by reaction (I) for different substituents Y at a silicon atom. It can be seen that the kinetic curves are linearized in the coordinates of a second-order reaction:

$$-dN/dt = k_1 N P_{\text{N}_2\text{O}},$$

where k_1 is the rate constant of reaction (I) in the forward direction and N is the concentration of silicon-centered radicals. A decrease in the pressure over a sample by ~ 5 times (for the reaction with the $(\equiv\text{Si}-\text{O})_2(\text{HO})\text{Si}^\bullet$ radical) resulted in a proportional decrease in the rate of the process (curves 2 and 3 in Fig. 11). That is, the apparent rate constant is independent of the gas pressure over the sample. This provides additional evidence for the kinetics control of the reaction. In the experimental setup that we used, diffusional limitations reveal themselves when the apparent rate constant is higher than $3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The values of rate constants of reaction (I) for different radicals are presented in Table 4. They increase in the series $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet$, $(\equiv\text{Si}-\text{O})_2(\text{HO})\text{Si}^\bullet$, and $(\equiv\text{Si}-\text{O})_2(\text{H})\text{Si}^\bullet$. It is interesting to note that their reactivities in hydrogen atom abstraction from the hydrogen molecule change in the opposite order [40].

The calculated value of the preexponential factor of the model reaction $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$ is $k_1^0(298 \text{ K}) = 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value enabled us to estimate the activation energy of reaction (I): 6–6.5 kcal/mol.

Table 1 shows the calculated activation energy of this reaction with different radicals. For the $\text{H} + \text{N}_2\text{O}$ system, the activation energy of this reaction is 9 kcal/mol [15]. Calculations by Durant [19] and Walsh [20] and our calculations at the G2MP2 level gave a close value of 8.4 kcal/mol for the activation energy. Calculations at the DFT level gave a 3 kcal/mol lower height of the activation barrier. The corrected value of the activation energy of this reaction for the model $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$ system is 5 kcal/mol (Table 1). This fact agrees well with experimental estimates. Thus, transition from the H atom to silicon-centered radical results

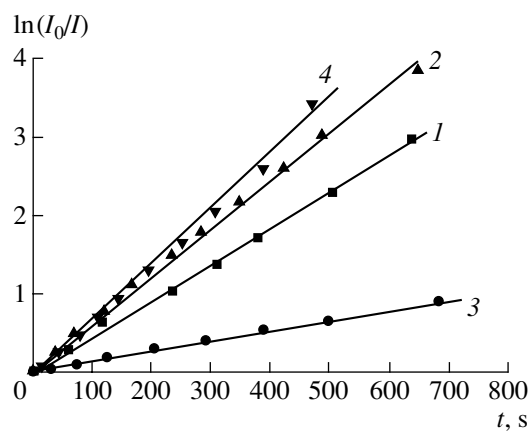


Fig. 11. Semilogarithmic anamorphoses of the curves of radical $(\equiv\text{Si}-\text{O})_2\text{Y Si}^\bullet$ decay in reaction (I) at 298 K for Y: (1) $\equiv\text{Si}-\text{O}$ ($P(\text{N}_2\text{O}) = 2.5 \times 10^{-2}$ torr); (2, 3) HO ($P(\text{N}_2\text{O}) = 2.84 \times 10^{-2}$ and 5.25×10^{-3} torr), respectively; and (4) H ($P_{\text{N}_2\text{O}} = 2.5 \times 10^{-2}$ torr); I_0 and I are the initial and current intensities of the corresponding radicals.

in a decrease in the activation energy of nitrous oxide addition and the formation of more firmly bound free-radical complex.

Figure 12 shows kinetic curves for the decomposition of radicals $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ by reaction (II). The kinetics of this reaction was monitored by the rate of gaseous N_2 formation. The reaction follows the first-order rate law, and the rate constants determined from the slopes of straight lines are listed in Table 4.

The formation of final products of this reaction (the oxy radical and the nitrogen molecule) by the cleavage of one of the chemical bonds in the radical $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ is impossible. The rearrangement is more complicated.

Table 4. Rate constants of reactions in the systems $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet + \text{N}_2\text{O}$ and $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet + \text{N}_2\text{O}$

Reaction	$T, \text{ K}$	Rate constant*
$(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet + \text{N}_2\text{O} \longrightarrow (\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$	298	$(5.7 \pm 0.3) \times 10^{-18}$
$(\equiv\text{Si}-\text{O})_2\text{Si}^\bullet-\text{OH} + \text{N}_2\text{O} \longrightarrow (\equiv\text{Si}-\text{O})_2(\text{HO})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$	298	$(7.7 \pm 0.5) \times 10^{-18}$
$(\equiv\text{Si}-\text{O})_2\text{Si}^\bullet-\text{H} + \text{N}_2\text{O} \longrightarrow (\equiv\text{Si}-\text{O})_2(\text{H})\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$	298	$(8.7 \pm 0.3) \times 10^{-18}$
$(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet \longrightarrow (\equiv\text{Si}-\text{O})_3\text{Si}-\text{O}^\bullet + \text{N}_2$	371	$(3.0 \pm 0.2) \times 10^{-5}$
	402	$(4.2 \pm 0.2) \times 10^{-4}$
$(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet + \text{N}_2\text{O} \longrightarrow (\equiv\text{Ge}-\text{O})_3\text{Ge}-\text{O}^\bullet + \text{N}_2$	348	$(1.9 \pm 0.2) \times 10^{-21}$
	393	$(9.1 \pm 0.5) \times 10^{-21}$
	438	$(1.2 \pm 0.2) \times 10^{-19}$

* The rate constants of bimolecular reactions are given in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and those of unimolecular reactions are in s^{-1} .

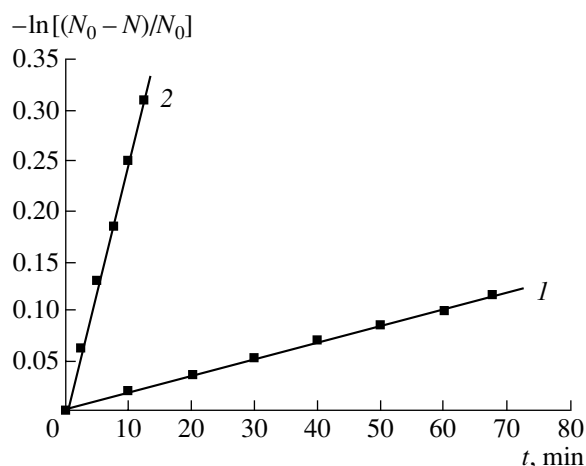


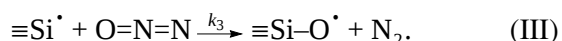
Fig. 12. Kinetic curves for a decrease in the concentration of the radicals $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ in reaction (II) at (1) 371 and (2) 402 K.

The structure of the transition state for the transformation of the radical $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ is shown in Fig. 1e.

The preexponential factor of the reaction $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet \rightarrow \text{TS} \rightarrow \text{F}_3\text{Si}-\text{O}^\bullet + \text{N}_2$ was $k_2^0 = 3 \times 10^{12} \text{ s}^{-1}$ (calculation). Then, from the measured values of the rate constant (II), we estimated that the activation energy is 29 kcal/mol. According to the calculations, the activation energy of radical $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ decomposition is 24.5 kcal/mol (see Table 1).

The $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical can decompose and eliminate a nitrous oxide molecule by the reaction reverse to its formation. In the study of thermal decomposition of these radicals, we did not register the reduction of silicon-centered radicals (ESR measurements). Taking into account possible experimental errors in rate constant measurements, this means that the ratio of the corresponding rate constants is $k_2/k_{-1} = (k_2^0/k_{-1}^0) \exp((E_{-1} - E_2)/RT) \geq 20$. The value of the preexponential factor k_{-1}^0 for nitrogen molecule abstraction from the $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical was $5.5 \times 10^{13} \text{ s}^{-1}$ (calculation). Taking into account the above values of preexponential factors we obtain $(E_{-1} - E_2) \geq 4.5 \text{ kcal/mol}$. Calculation also suggests that the activation energy of isomerization with the decomposition of the $\text{F}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical is lower (by 8.7 kcal/mol) than the activation energy for the elimination of a nitrous oxide molecule (Table 1).

To complete this section, let us dwell on the direct abstraction of the oxygen atom from nitrous oxide by a radical:

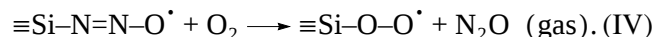


This is the main direction when N_2O reacts with the $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ radical (see below) and with the hydrogen atom at temperatures above 1000 K [12–16]. The structure of the transition state for this channel of transformations of the $\text{F}_3\text{Si}^\bullet$ radical is shown in Fig. 1f.

At temperatures around 300 K, this reaction with the $(\equiv\text{Si}-\text{O})_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical was not registered experimentally. This means that the ratio of the rate constants of bimolecular reactions of addition and abstraction k_1/k_3 is greater or equal to 25. Calculation showed that $k_1^0/k_3^0 \approx 1$. Then, $\exp((E_3 - E_1)/RT) \geq 25$ and $(E_3 - E_1) \geq 2 \text{ kcal/mol}$. The calculated activation energy of the addition in the model system is lower by 5.6 kcal/mol (see Table 1).

4. REACTIVITY OF $\text{X}-\text{N}=\text{N}-\text{O}^\bullet$ RADICALS

Radicals **I**, **II**, and **III** react with molecular oxygen. This process at 300 K is accompanied by (1) oxygen chemisorption and the appearance of N_2O in the gas phase in comparable amounts, (2) almost complete transformation of the $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radicals into the peroxy radicals $\equiv\text{Si}-\text{O}-\text{O}^\bullet$ (ESR data); (3) the absence of ^{18}O in nitrous oxide when the reaction is carried out in an $^{18}\text{O}_2$ atmosphere (mass spectrometric data). Therefore, under these conditions molecular oxygen displaces nitrous oxide in the radical center:



The estimated activation energy of reaction (IV) is $7 \pm 1 \text{ kcal/mol}$ (estimates from experimental data).

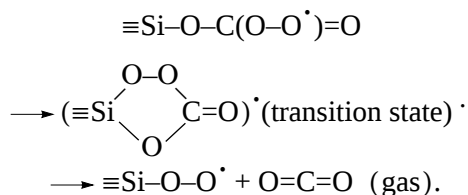
The enthalpies of reactions (I) and (IV) were measured by the calorimetric method. The procedure was described in [41]. In these experiments, we used samples of mechanically activated silica. The results of measurements are summarized in Table 5. Two series of measurements were carried out (series 1 and 2 in the table). The chemisorption of gases was carried out in portions. The table shows the amount of chemisorbed molecules, the structure of radical products, and the reaction enthalpy. After chemisorption of nitrous oxide, the surface was treated with oxygen. Oxygen absorption was accompanied by the desorption of nitrous oxide, which was collected using a trap cooled with liquid nitrogen. These data suggest that the amounts of these molecules are close.

The heats of reactions (I) and (IV) were 33 ± 2 and $27 \pm 2 \text{ kcal/mol}$, respectively. The overall heat of these two processes equals the heat of O_2 chemisorption on the radical centers $(\equiv\text{Si}-\text{O})_3\text{Si}^\bullet$ and it was experimentally

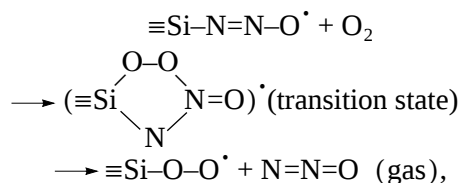
measured by the calorimetric method (60 ± 2 kcal/mol) [41]. That is, these two measurements agree very well.

The calculated heat of N_2O addition to the radical $\text{F}_3\text{Si}^\bullet$ (0 K) is 28.2 kcal/mol (see Table 1). The heat of the reaction $\text{F}_3\text{Si}^\bullet + \text{O}_2 \rightarrow \text{F}_3\text{Si-O-O}^\bullet$ at 0 K is 62.1 kcal/mol (calculation at the G2MP2 level [22]). Therefore, the heat of reaction $\text{F}_3\text{Si-N=N-O}^\bullet + \text{O}_2 \rightarrow \text{F}_3\text{Si-O-O}^\bullet + \text{N}_2\text{O}$ (gas) is 33.9 kcal/mol. Comparison of experimental and calculated data suggests that the calculated heat of nitrous oxide addition to silicon-centered radical is underestimated by 3–4 kcal/mol.

Let us discuss the structure of the possible transition state for nitrous oxide displacement by molecular oxygen at the silicon center (reaction (IV)). The reaction of the isoelectronic radical $\equiv\text{Si-O-C}^\bullet=\text{O}$ with oxygen molecule is also accompanied by the displacement of the O=C=O molecule from the silicon center and by the formation of peroxy radical $\equiv\text{Si-O-O}^\bullet$ [42]. The intermediate product of this reaction is the $\equiv\text{Si-O-C}(\text{O-O}^\bullet)=\text{O}$ radical, which was registered by the ESR method. The formation of final products occurs by the isomerization with the decomposition of this complex and occurs via a cyclic transition state with a five-coordinated silicon atom:



We assume that the displacement of nitrous oxide from the radical center occurs via a similar five-membered transition state



but without the peroxy radical. At 77–300 K, the formation of an intermediate paramagnetic complex between the $\equiv\text{Si-N=N-O}^\bullet$ radical and oxygen molecule was not detected by the ESR method.

We applied the methods of quantum chemistry to the simpler radical of this type $\text{H-N=N-O}^\bullet$ to analyze the possibility for the formation of its complex with the O_2 molecule. Nitrogen and oxygen atoms in the radical were considered as possible sites for the addition of the oxygen molecule. The calculations did not suggest the formation of a stable compound in any of the cases. The O_2 molecule initially placed at a distance equal to the length of a “typical” chemical bond, during optimization moved away from the radical center to the distance corresponding to the weak adsorption complex. The only exothermic channel for the reaction is the abstraction of a hydrogen atom by the oxygen molecule:

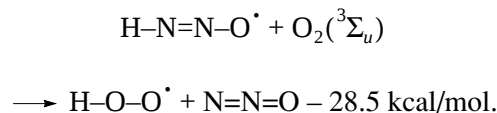


Table 5. Results of microcalorimetric measurements of the heats of reactions $(\equiv\text{Si-O})_3\text{Si}^\bullet + \text{N}_2\text{O} \rightarrow (\equiv\text{Si-O})_3\text{Si-N=N-O}^\bullet$ (I) and $\equiv\text{Si-N=N-O}^\bullet + \text{O}_2 \rightarrow \equiv\text{Si-O-O}^\bullet + \text{N}_2\text{O}$ (gas) (IV) ($T = 300$ K)

Experiment	Reaction	Number of chemisorbed gaseous molecules, $\times 10^{-17}$	Number of formed product molecules, $\times 10^{-17}$	Products structure	Q, kcal/mol
Series 1	(I)	N_2O 2.5	–	$\equiv\text{Si-N=N-O}^\bullet$	33.0
	(I)	N_2O 2.1	–	$\equiv\text{Si-N=N-O}^\bullet$	33.5
	(IV)	O_2 1.9	N_2O 1.9	$\equiv\text{Si-O-O}^\bullet$	26.0
	(IV)	O_2 1.8	N_2O 2.0	$\equiv\text{Si-O-O}^\bullet$	29.0
Series 2	(I)	N_2O 2.2	–	$\equiv\text{Si-N=N-O}^\bullet$	35.0
	(I)	N_2O 3.0	–	$\equiv\text{Si-N=N-O}^\bullet$	30.0
	(IV)	O_2 –	N_2O 3.0	$\equiv\text{Si-O-O}^\bullet$	27.0
	(IV)	O_2 –	N_2O 1.3	$\equiv\text{Si-O-O}^\bullet$	25.0

The calculated value of the enthalpy of this reaction is close to the experimentally determined value for the enthalpy of reaction (IV).

The delocalization of the spin density in free radicals (see data of Table 3) usually results in a decrease in their reactivity. The low reactivity of the radicals $X-N=N-O^{\bullet}$ is also evident from the results of the calculation of the heats of the addition of another electronegative atom, fluorine, to the $H-N=N-O^{\bullet}$ radical. Possible products of this reaction are $HFN-N=O$, $HN=FN=O$, and $HN=N-OF$. According to the calculation at the G2MP2 level, the heats of these reactions are comparatively low (-44.8 , -55.8 , and -17.5 kcal/mol, respectively). Thus, the preferable site for the addition of an electronegative substituent is the central nitrogen atom. As in the case of molecular oxygen, the disproportionation reaction $H-N=N-O^{\bullet} + F \rightarrow HF + N=N=O - 114.8$ kcal/mol is thermochemically preferable.

Radicals considered here are close to allyl radicals in their reactivity in the reactions of hydrogen atom abstraction; that is, they are poorly active. The heats of reactions of hydrogen atom addition to the $H-N=N-O^{\bullet}$ radical with the formation of $H_2N-N=O$, $HN=HN=O$ and $HN=N-OH$ products calculated at the G2MP2 level are -81.1 , -67.4 , and -80.6 kcal/mol. The heat of the reaction $H_2N^{\bullet} + H \rightarrow H_3N$ calculated at the G2MP2 level is $\Delta H(0K) = 106.7$ kcal/mol compares well with an experimental value of 108.3 kcal/mol [1].

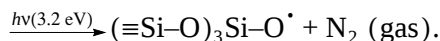
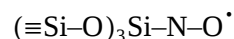
Thus, although according to quantum chemical calculation the highest spin density is localized on the central nitrogen atom (see Table 3), this $H-N$ bond is the weakest. As a result, the activation energy of endothermic reactions $H-N=N-O^{\bullet} + H_2 \rightarrow H + H_2N-N=O$ and $H-N=N-O^{\bullet} + H_2 \rightarrow H + HN=N-OH$ are higher than 23 kcal/mol (the values of their heat effects). To compare: the experimental activation energy of the reaction $CH_2=CH-CH_2^{\bullet} + H_2 \rightarrow CH_3-CH=CH_2 + H$ is 19 kcal/mol and the reaction heat is 18 kcal/mol [1]. The calculated heat of the disproportionation reaction $H-N=N-O^{\bullet} + H \rightarrow H_2 + N=N=O$ is 82.3 kcal/mol (at the G2MP2 level).

5. PHOTOREACTIONS OF $\equiv Si-N=N-O^{\bullet}$ RADICALS

We studied the photostability of the $(\equiv Si-O)_3Si-N=N-O^{\bullet}$ radicals excited by energy corresponding to long-wave absorption (3.2 eV). Photolysis of the sample was carried out at 300 K using light from a DRSh-1000 mercury lamp through a water filter and an FS-1 filter whose spectral characteristic is shown in Fig. 10b with a dashed line. To prevent heating during photolysis,

the ampule with a sample was filled with helium (1 torr).

Photolysis is accompanied by a decrease in the concentration of the $(\equiv Si-O)_3Si-N=N-O^{\bullet}$ radicals (as controlled by ESR), the quantitative evolution of gaseous molecular nitrogen (as controlled by the volumetric method), and the appearance of paramagnetic centers that are the $(\equiv Si-O)_3Si-O^{\bullet}$ radicals. The formation of these radicals was controlled by different methods: (1) the luminescence method was used to control an increase in the intensity of red luminescence in the sample during photolysis (luminescence was initiated by low-intensity UV light with an energy of $4-5$ eV [43] and (2) by transforming the oxy radicals into a form that is more convenient of ESR registration ($\equiv Si-O)_3Si-O-C^{\bullet}=O$ (treatment with CO molecules [4]). We did not register the formation of any other products of $(\equiv Si-O)_3Si-N=N-O^{\bullet}$ photoreactions. Thus, as in the case of thermal decomposition, the absorption of light with energy corresponding to the long-wave absorption band results in their photodecomposition according to the scheme



We also studied photoreactions of the radicals $(\equiv Si-O)_2(DO)Si-N=N-O^{\bullet}$ and $(\equiv Si-O)_2(D)Si-N=N-O^{\bullet}$ on their excitation by light with energy corresponding to the long-wave optical absorption band (FS-1 filter, 300 K). The main channel for radical phototransformation remained their decomposition with the formation of the oxy radical and a nitrogen molecule. However, in addition to these products, we registered the abstraction of N_2O molecules (volumetric registration) and the reduction of radicals $(\equiv Si-O)_2(DO)Si^{\bullet}$ or $(\equiv Si-O)_2(D)Si^{\bullet}$ (ESR registration). The relative yield of the second channel of phototransformation is 0.05 ± 0.01 and 0.25 ± 0.02 for radicals $(\equiv Si-O)_2(DO)Si-N=N-O^{\bullet}$ and $(\equiv Si-O)_2(D)Si-N=N-O^{\bullet}$, respectively.

Thus, in the series of radicals $(\equiv Si-O)_3Si-N=N-O^{\bullet}$, $(\equiv Si-O)_2(DO)Si-N=N-O^{\bullet}$, and $(\equiv Si-O)_2(D)Si-N=N-O^{\bullet}$, the yield of the second channel of photoreaction increases from zero to 0.25 . This correlates with an expected decrease in the strength of the $Si-N$ bond in this series of radicals [22]. Because the photoabstraction of the nitrous oxide molecule can occur only by the cleavage of the $Si-N$ bond, the above experimental data suggest that the relaxation of the structure of electronically excited radical is accompanied by the elongation of the $Si-N$ bond.

The formation of oxy radicals and nitrogen molecules in thermal dissociation and photodissociation of the $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radicals suggests that there are common features in the mechanisms of these processes. Because the formation of final products in the thermally activated reaction occurs via a cyclic transition state, we conjecture that photodissociation occurs via a geometrically similar structure. According to experimental data, the direction of the photoreaction is independent of temperature (77 and 300 K). However, only the *cis*-conformation of the $\equiv\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ radical may lead to the transition state corresponding to isomerization with the decomposition (see Section 1), whereas only the *trans*-conformation of the radical is populated at 77 K since it is more stable than the *cis*-conformation by almost 6.5 kcal/mol (Table 1). With an increase in the length of the Si–N bond, the *cis*-conformation of the radical (see Section 1) becomes more favorable. This results in the following mechanism of the radical photodecomposition. The relaxation of electronically excited state of the radical is accompanied by the elongation of the Si–N bond and an increase in the ONN angle. When the SiNNO atoms acquire the *cis*-configuration, the ONN angle continues to decrease and oxygen and silicon atoms approach each other. As this takes place, the structure similar to the transition state of the thermally activated decomposition of the radical is formed. To check the proposed hypothesis, it is necessary to determine the nature of the electronic transition responsible for the long-wave band of their optical absorption and the nature of the relaxation of the radical structure in this excited state.

6. SYSTEM $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$

The silyl radical is an intermediate in the process of silane combustion and oxidation, and many experimental and theoretical studies have been devoted to this radical. However, we know of no study devoted to the $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$ system. In this section and in Section 9, we report data on this system obtained with quantum chemical methods (Fig. 1, Table 1).

The silyl radical forms a rather stable complex (18 kcal/mol) with the nitrous oxide molecule (Table 1). Its stability is ~ 10 kcal/mol lower than the stability of the complex with the $\text{F}_3\text{Si}^\bullet$ radical. The expected spectral characteristics of this complex are reported in Section 9 of this paper.

Two competing channels for the decomposition of this complex exist: (1) the abstraction of the nitrous oxide molecule and (2) its isomerization with decomposition resulting in the formation of the oxy radical and a nitrous oxide molecule. These channels have close activation energies. The activation energy of direct oxygen atom abstraction is ~ 4 kcal/mol higher. Thus, the transition states for different channels of

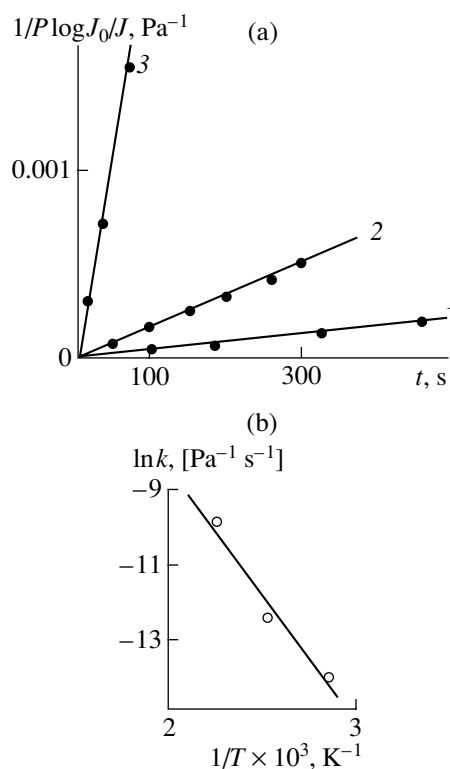


Fig. 13. Kinetics of the reaction $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet + \text{N}_2\text{O} \longrightarrow (\equiv\text{Ge}-\text{O})_3\text{Ge}-\text{O}^\bullet + \text{N}_2$: (a) changes in the concentrations (J) of the radicals $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ at (1) 348, (2) 393, and (3) 438 K; P is the N_2O pressure, Pa and (b) Arrhenius plot of the rate constant.

transformations in the $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$ system are similar in energies (Table 1). For the processes with the $\text{F}_3\text{Si}^\bullet$ radical the differences are much more pronounced (Table 1).

Based on data obtained in this work, we assume that in the $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$ system at moderate temperatures the formation of products (the oxy radical and molecular nitrogen) largely occurs via the step of complex formation. Note that the main minimum on the potential energy surface for the $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$ system corresponds to the formation of other products $\text{H}_2\text{Si}^\bullet-\text{OH} + \text{N}_2$. The isomerization of the oxy radical $\text{H}_3\text{Si}-\text{O}^\bullet \longrightarrow \text{H}_2\text{Si}^\bullet-\text{OH}$ is accompanied by an exo-effect of 27.4 kcal/mol (calculated at the G2MP2 level).

7. REACTION $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet + \text{N}_2\text{O} \longrightarrow (\equiv\text{Ge}-\text{O})_3\text{Ge}-\text{O}^\bullet + \text{N}_2$

At 300 K and a nitrous oxide pressure of several torrs (and exposure of several tens of minutes), the

$(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ radicals stabilized on the surface of mechanically activated GeO_2 do not react with gaseous molecules (as controlled by ESR). The reaction begins with an increase in temperature, and the concentration of radicals is accompanied by the appearance of approximately the same amount of N_2 molecules in the gas phase and oxy radicals. That is, under these conditions, the following process occurs [10, 11]:

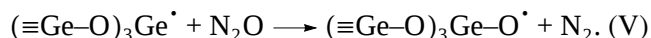


Figure 13a shows the kinetic curves for the changes in the concentration of the $(\equiv\text{Ge}-\text{O})_3\text{Ge}^\bullet$ radicals (controlled by ESR) during this reaction [44, 45]. The obtained experimental data can be described by a linear plot in the coordinates of the first-order reaction. The reaction rate constants determined from the slopes of these linear plots at different temperatures are shown in Table 4. Figure 13b shows them in the coordinates of the Arrhenius equation from which we obtain $k = (9.4 \pm 0.5) \times 10^{-13} \exp(-(14 \pm 0.5)/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (the activation energy is in kcal/mol).

Unlike for silicon-centered radicals, no free-radical complex was experimentally registered for this reaction. The results of potential energy surface calculation of the model system $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O}$ are summarized in Table 1. For this system, we found the same minima and transition states on the potential energy surface as for the $\text{F}_3\text{Si}^\bullet + \text{N}_2\text{O}$ system, but the position of some structures on the energy scale changed substantially. First, the strength of the radical complex with a nitrous oxide increased by 26 kcal/mol and the activation energy of its formation increased. This leads to a decrease in the equilibrium concentration of such a complex (if it is formed) under normal conditions and it is necessary to increase substantially the N_2O pressure over the sample. However, an important point is that the activation energy of isomerization with decomposition drastically increases at the same time. In this case, the energy of the transition state is much higher than for the reaction of direct oxygen atom abstraction.

Table 6. Expected radiospectroscopic characteristics of radicals $\text{H}-\text{N}=\text{N}-\text{O}^\bullet$ and $\text{H}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$

Parameter	$\text{H}-\text{N}(2)=\text{N}(1)-\text{O}^\bullet$	$\text{H}_3\text{Si}-\text{N}(2)=\text{N}(1)-\text{O}^\bullet$
g_{iso}	2.001	2.001
$a_{\text{iso}}(^{14}\text{N}(1)), \text{G}$	31	34
$a_{\text{iso}}(^{14}\text{N}(2)), \text{G}$	-2.9	-3.5
$a_{\text{iso}}(^1\text{H}), \text{G}$	21	$\leq 4(a_{\text{iso}}(^1\text{H}))$
$a_{\text{iso}}(^{29}\text{Si}), \text{G}$	—	14

As a result, in this system, the oxidation of radical centers occurs via the mechanism of the direct abstraction of germanium-centered radical of the oxygen atom from the N_2O molecule. For the reaction $\text{F}_3\text{Ge}^\bullet + \text{N}_2\text{O} \longrightarrow \text{F}_3\text{Ge}-\text{O}^\bullet + \text{N}_2$, the calculated activation energy (13.1 kcal/mol, Table 1) agrees well with experimental data for reaction (V). Acceptable agreement between experimental (17 kcal/mol [15]) and calculated (Table 1) values was achieved also for the activation energy of direct oxygen atom abstraction by H from a nitrous oxide molecule.

8. REACTION $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O} \longrightarrow \text{H}_3\text{C}-\text{O}^\bullet + \text{N}_2$

Results of quantum chemical calculation of the potential energy surface of this system (Table 1) prove that, in the case of methyl radical, the main channel of the reaction with the N_2O molecule is the reaction of direct oxygen abstraction. According to the calculation, the activation energy of this reaction is ~ 25 kcal/mol. Falkoner *et al.* [17] measured the rate constant of the reaction $\text{H}_3\text{C}^\bullet + \text{N}_2\text{O} \longrightarrow \text{H}_3\text{C}-\text{O}^\bullet + \text{N}_2$ at 873 K: $2.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We calculated the value of the preexponential factor for this reaction: $2.24 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The activation energy estimated from these two values is 23.2 kcal/mol, which agrees well with the value calculated using quantum chemical methods.

According to the calculation, isomerization with the decomposition of the $\text{H}_3\text{C}-\text{N}=\text{N}-\text{O}^\bullet$ complex has a much higher activation energy than the activation energies of analogous reactions in the systems under study (Table 1). Isomerization with decomposition occurs via a four-membered cyclic state, and the atoms of H, C, Si, and Ge are at the states with high coordination numbers (2 in the case of H and 5 in the case of C, Si, and Ge). The differences in the activation energies of similar rearrangements reflect chemical properties of these elements: the transition of the carbon atom to the pentacoordinated state requires much higher energy expenses than the transitions of H, Si, and Ge to the states with "unusual" coordination numbers. In the case of hydrogen, this is due to its spatial symmetry and the possibility of attacking it from the required side. In the case of silicon and germanium atoms, this is due to the higher mobility of their valence electrons that makes the structures with high coordination numbers possible.

9. EXPECTED SPECTRAL CHARACTERISTICS OF RADICALS $\text{H}-\text{N}=\text{N}-\text{O}^\bullet$ AND $\text{H}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$

Radicals $\text{H}-\text{N}=\text{N}-\text{O}^\bullet$ and $\text{H}_3\text{Si}-\text{N}=\text{N}-\text{O}^\bullet$ have not been experimentally registered. Below we report their expected spectral characteristics (for the second channel the values are given in parentheses): radiospectroscopic characteristics (Table 6) and absorption in IR

and optical ranges. IR absorption should be expected at 1622 (1600) (a very intense band) and 1295 (1315) cm^{-1} (according to the calculation, the intensity of this band is approximately two times lower for the $\text{H-N=N-O}^\bullet$ radical and 10 times lower for the $\text{H}_3\text{Si-N=N-O}^\bullet$ radical), and the bands of optical absorption should have maxima near 3, 5, and >6 eV (the most intense). These estimates are based on experimental data obtained for the $(\equiv\text{Si-O})_3\text{Si-N=N-O}^\bullet$ radical and corrected according to the results of quantum chemical calculations. The scaling factor was the ratio of calculated values for $\text{F}_3\text{Si-N=N-O}^\bullet$ (the model of $(\equiv\text{Si-O})_3\text{Si-N=N-O}^\bullet$) and $\text{H-N(2)=N(1)-O}^\bullet$ ($\text{H}_3\text{Si-N=N-O}^\bullet$).

CONCLUSION

The formation of final products in the systems $\text{X}^\bullet + \text{N}_2\text{O}$ may occur via two channels. The first one is associated with the formation of a metastable complex (reaction (I)) and its further decomposition (reaction (II)). The second channel is the direct abstraction of the oxygen atom by the radical $\text{X}^\bullet$ (reaction (III)). Depending on the structure of $\text{X}^\bullet$, the role of various channels to the formation of final oxidation products changes. In the case of the radical $\equiv\text{Si}^\bullet$, reactions (I) and (II) play the main role. The latter reaction occurs via the four-membered cyclic transition state (TS-3) in which the silicon atom is pentacoordinated. The experimentally determined selectivity of this process is at least 95%. This points to the fact that the activation energy of this reaction is lower than for the reverse reaction of nitrous oxide elimination. The second channel (reaction (III)) for this system is characterized by a higher activation energy and is less important at 300–450 K. Figure 14 shows the energy diagram for the $(\equiv\text{Si-O})_3\text{HSi}^\bullet + \text{N}_2\text{O}$ system constructed on the basis of experimental and calculated data.

For the $(\equiv\text{Ge-O})_3\text{Ge}^\bullet$ radical, the main direction of the process is reaction (III). According to the calculations, the $\equiv\text{Ge-N=N-O}^\bullet$ complex is unstable and the reaction of its formation is almost thermoneutral. The transition state for its isomerization with decomposition is higher than for the process with direct oxygen abstraction. A similar situation is observed for the process with the participation of the methyl radical, but in this case the activation energy of reaction (II) is especially high.

Calculations showed that the activation energy of $\text{F}_3\text{Ge}^\bullet$ oxidation is lower than for the methyl radical (see Table 1). On the other hand, the reaction of methyl radical oxidation is characterized by the higher heat effect. We suppose that electrostatic interaction stabilizes the transition state in the case of the germeryl radi-

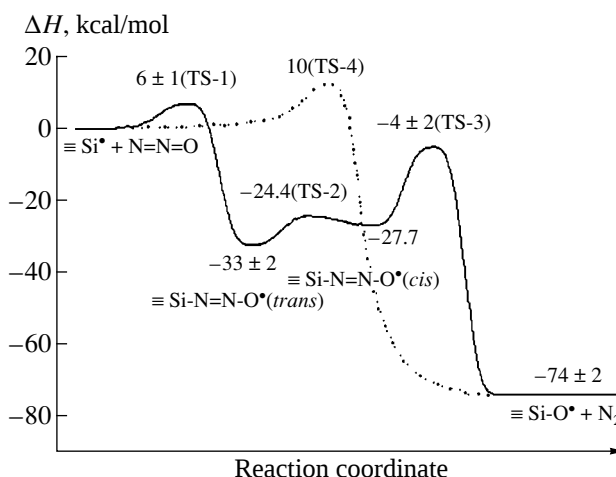


Fig. 14. Potential energy diagram for the system $(\equiv\text{Si-O})_3\text{Si}^\bullet + \text{N}_2\text{O}$ (for experimentally determined values, an error is indicated). The solid line shows the pathway for the formation of products $(\equiv\text{Si-O})_3\text{Si-O}^\bullet + \text{N}_2$ via an intermediate complex. The dashed line shows the pathway for the direct oxygen abstraction from nitrous oxide.

cal. For the reaction with the $\text{F}_3\text{Ge}^\bullet$ radical, a positive charge of $-1.35e$ is localized at the Ge atom, whereas a positive charge of $0.34e$ is localized at the oxygen atom. In the transition state for the reaction with participation of the methyl radical, both carbon and oxygen atoms have similar negative charges ($\sim 0.28e$).

In the case of a hydrogen atom, the transition states of both channels have similar energies (literature data and Table 1). For the $\text{H}_3\text{Si}^\bullet$ radical the channel associated with the formation and decomposition of the complex is more favorable. For the systems $\text{H} + \text{N}_2\text{O}$ and $\text{H}_3\text{Si}^\bullet + \text{N}_2\text{O}$, the heats of complex formation and product formation are close, whereas the energies of transition states (especially for reactions (II) and (III)) are noticeably different. The differences in the properties of hydrogen and silicon atoms reveal themselves in transition states better than in stable structures.

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