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# Interaction of Nitromethane with Modified Paramagnetic Defects on a Thermochemically Activated Silica Surface

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**Abstract**—It was found that the interaction of the modified paramagnetic defects $\equiv SiO(CH_2)_nC^{\bullet}H_2$ ($n = 0.1$) with nitromethane on a thermochemically activated silica surface at 300 K results in the formation of the following nitroxyl radicals: $\equiv SiO(CH_2)_nCH_2ON(O^{\bullet})CH_3$ and $\equiv SiO(CH_2)_nCH_2N(O^{\bullet})CH_3$. It was suggested that these radicals are the products of two different reactions of the modified paramagnetic defects: the first results from a reaction with free nitromethane; the second, from a reaction with nitromethane bound as complexes with diamagnetic surface defects.

## INTRODUCTION

Matrix stabilization of radicals on an activated silica surface made it possible to obtain unique information on the mechanisms of thermal and photochemical reactions of various radicals such as alkyl, vinyl, allyl, cyclohexadienyl, peroxy, oxysulfinyl, and sulfonyl [1]. In the majority of relevant publications (for example, [2]), it was suggested that a surface activated by various techniques is inert toward tested intermediates and has no effect on the direction and efficiency of radical reactions. However, with the use of the photoreactions of various alkylperoxy radicals as an example, we were the first to find [3] that, in fact, an activated silica surface affects the selection of particular reaction paths of radicals grafted onto the surface.

In this work, we studied the reactions of nitro compounds as test materials because of the circumstances described below. First, it is well known that aliphatic nitro compounds are used as spin traps [4, 5]. Consequently, they react efficiently with paramagnetic species, in particular, with the intrinsic paramagnetic defects of silicon dioxide. Second, nitroxyl radicals, which are widely used as paramagnetic probes, are the products of reactions between nitro compounds and paramagnetic species.

Previously [6], we first obtained nitroxyl radicals grafted directly onto the silica surface without an organic bridge by the interaction of nitromethane with silyl radicals ($\equiv Si^{\bullet}$). These nitroxyl radicals may potentially be used as probes for surface layers, in particular, adsorption layers.

The aim of this work was to study the interaction of nitromethane with modified paramagnetic defects on an activated silica surface and the mechanisms of the reactions therefrom.

## EXPERIMENTAL

Aerosil A-175 thermochemically activated according to two published procedures [7, 8] was used in this study. One of these procedures [7] consists of high-temperature pyrolysis of premethoxylated Aerosil to produce the formation and stabilization of paramagnetic surface defects, such as silyl radicals, on the activated surface (reactive silica, RSi). The other procedure [8], which is a modification of the above, includes an additional stage of annealing in an oxygen atmosphere after high-temperature pyrolysis. This treatment increases (by more than one order of magnitude) the concentration of paramagnetic surface defects in the form of oxysilyl radicals $\equiv SiO^{\bullet}$ (modified surface of reactive silica, modified RSi).

The silica surface was activated so that it always contained paramagnetic defects of only one type (i.e., either silyl or oxysilyl radicals) regardless of the activation procedure. The radicals were converted from one type to another according to well-known procedures [9, 10].

Modified paramagnetic defects ($\equiv SiOC^{\bullet}H_2$ and $\equiv SiOCH_2C^{\bullet}H_2$) were obtained either by adding gas-phase formaldehyde to $\equiv Si^{\bullet}$ at room temperature or by adding ethylene to $\equiv Si^{\bullet}$ at 190 K. Nitromethane was also made to react with the modified paramagnetic defects from a gas phase at room temperature. The amount of gaseous reactants brought into contact with the activated silica surface was monitored with the use of a precalibrated Pirani gauge. Nitromethane quantitatively reacts with modified paramagnetic defects on the RSi surface, whereas the reaction on the modified RSi

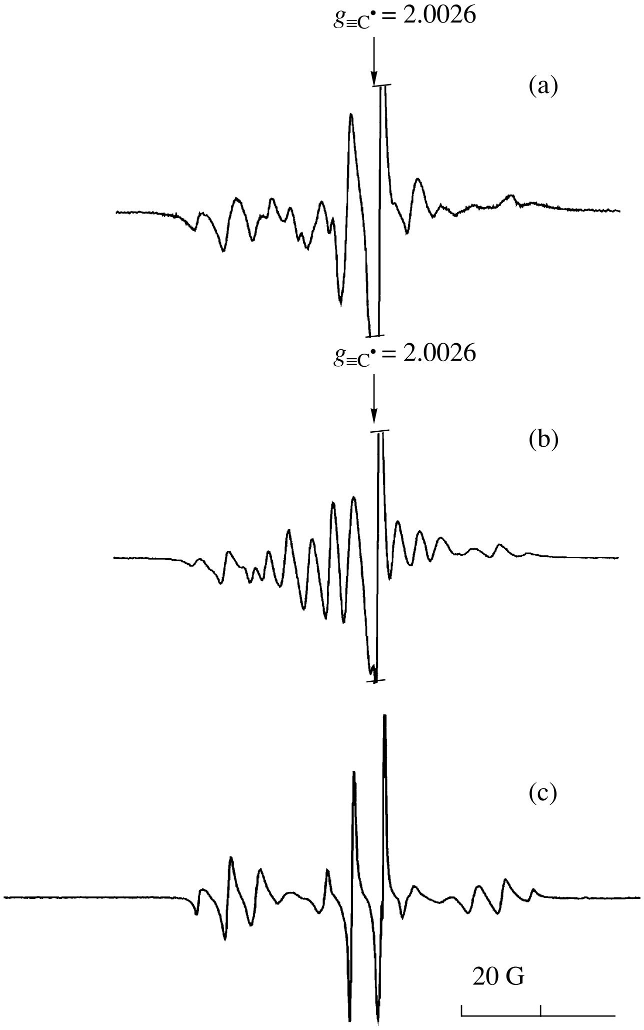


**Fig. 1.** ESR spectra of the paramagnetic reaction products of $\equiv SiOC^\bullet H_2$ radicals with nitromethane at 300 K on (a) RSi and (b) modified RSi; (c) the ESR spectrum of the radical $\equiv SiON(O^\bullet)CH_3$ [6].

surface is accompanied by a decrease in the concentration of paramagnetic centers by a factor of 2–4.

The ESR spectra were measured on a Varian E-3 radiospectrometer. The number of paramagnetic centers in a sample was determined with the use of a $CuCl_2 \cdot 2H_2O$ single crystal with a known number of Cu(II) ions as a standard sample. The central portions of the ESR spectra were distorted because of the superposition of a singlet signal due to carbon deposits ($\equiv C^\bullet$ with $g = 2.0026$, indicated by arrows in the figures) that are formed during silica surface activation.

The experimental ESR spectra were simulated with the use of the PEST WinSim program, assuming the isotropy of hyperfine coupling (HFC) constants.

## RESULTS

### *Nitromethane Reaction with the Modified Paramagnetic Defects $\equiv SiOC^\bullet H_2$*

The interaction of nitromethane with $\equiv SiOC^\bullet H_2$ resulted in the appearance of ESR spectra as the superposition of signals due to paramagnetic species of at least two types (Figs. 1a, 1b). In this case, the same paramagnetic species were formed regardless of the surface activation procedure; however, the quantitative ratios between them were different. The exposure of samples with different surface-activation procedures at ~370 K for a lapse of time (30–60 min) was accompanied by the decay of one of the radicals present in the mixture. As a result of this, the spectra of both samples became identical (Figs. 2a, 2b). In our opinion, this spectrum belongs to the nitroxyl radicals $\equiv SiOCH_2N(O^\bullet)CH_3$ (**I**). The best fit of the calculated ESR spectrum (Fig. 2c) with the experimental spectrum was attained at the HFC constants $a_N = 12$ G, $a_H(CH_3) = 11$ G, and $a_H(\alpha\text{-}CH_2) = 5$ G, which are consistent with published data for nitroxyl radicals (see the table).

In our opinion, radicals that decayed as the sample temperature increased from room temperature to ~370 K are also nitroxyl radicals, however, with the different structure $\equiv SiOCH_2ON(O^\bullet)CH_3$ (**II**). By analogy with the spectrum of the nitroxyl radicals $\equiv SiON(O^\bullet)CH_3$ [6] (Fig. 1c), the ESR spectrum of these radicals is a triplet of quartets. The outermost low-field components ascribed to **II** are clearly pronounced in the ESR spectrum obtained upon the interaction of nitromethane with $\equiv SiOC^\bullet H_2$ on RSi (Fig. 1a), and the found HFC constants ($a_N \approx 30$ G and $a_H(CH_3) \approx 8$ G) are consistent with analogous values for the structurally similar radicals $\equiv SiON(O^\bullet)CH_3$ and $RON(O^\bullet)R'$ (see the table).

It can be easily seen (Figs. 1a, 1b) that the concentration ratios between the different types of nitroxyl radicals are noticeably different for different surface activation procedures. Under the conditions of our experiments, [**I**]/[**II**] was ≈1/2 or ≈2/1 on RSi or modified RSi, respectively.

Thus, two types of nitroxyl radicals, **I** and **II**, are formed by the interaction of nitromethane with the modified paramagnetic defects $\equiv SiOC^\bullet H_2$ regardless of the procedure used for silica surface activation. The concentration ratios between these intermediates are different for different surface-activation procedures.

### *Nitromethane Reaction with the Modified Paramagnetic Defects* $\equiv SiOCH_2C^{\bullet}H_2$

Two types of radicals were also formed in the reaction of nitromethane with $\equiv SiOCH_2C^{\bullet}H_2$ on RSi (Fig. 3a). The exposure of samples at ~370 K for 30–60 min resulted in a change in the ESR spectrum (Fig. 3b) because of the decay of one of these radicals. The ESR spectrum of thermally stable (up to ~370 K) radicals is a multiplet of eight lines with a splitting of ~13 G. As distinct from RSi, in the reaction of nitromethane with $\equiv SiOCH_2C^{\bullet}H_2$ on modified RSi at 300 K, a paramagnetic species that gives a multiplet of eight lines with a splitting of ~11–12 G in the ESR spectrum was almost the only reaction product (Fig. 4a). This species remained unchanged when samples were subsequently heated up to 370 K (Fig. 4b).

To simplify the interpretation of this spectrum, which is difficult to analyze, and to determine the constant of the hyperfine interaction with hydrogen atoms of the methyl group, we obtained and investigated the ESR spectrum of the reaction product of $CD_3NO_2$ with $\equiv SiOCH_2C^{\bullet}H_2$ on modified RSi under analogous conditions (Fig. 5a). In our opinion, this spectrum can be attributed to the radicals $\equiv SiOCH_2CH_2N(O^{\bullet})CD_3$ on condition that the constants of HFC on nitrogen atoms and hydrogen atoms of the α-methylene group are similar (the shape of the spectrum indicates that the radical contains a nucleus with HFC anisotropy that was incompletely averaged under experimental conditions). We found by simulation (Fig. 5b) that the best agreement between experimental and calculated spectra was attained at the HFC constants $a_N = 15$ G and $a_H(\alpha\text{-}CH_2) = 13$ G. The hyperfine structure of the spectrum due to the interaction with deuterium nuclei was not observed because of a small HFC constant (≤2 G). On this basis, we ascribed the ESR spectrum of eight lines (Fig. 4a) to the nitroxyl radicals $\equiv SiOCH_2CH_2N(O^{\bullet})CH_3$ (**III**). The HFC constants for radical **III** were determined by a comparison between experimental and calculated spectra (Fig. 4). The ESR spectrum of radicals that are thermally unstable at 370 K on RSi, which was obtained by graphical subtraction, is analogous to the spectra of radicals **II** and $\equiv SiON(O^{\bullet})CH_3$ (Figs. 1c, 3c). We assigned this spectrum to the radical $\equiv SiOCH_2CH_2ON(O^{\bullet})CH_3$ (**IV**). The HFC constants for radical **IV** are given in the table. The concentration ratio between radicals formed on RSi was estimated at [**III**]/[**IV**] ≈ 1.5/1.

Thus, two types of nitroxyl radicals, **III** and **IV**, are formed by the interaction of nitromethane with the modified paramagnetic defects $\equiv SiOCH_2C^{\bullet}H_2$ on RSi, whereas only radicals of type **III** are formed on modified RSi ([**III**]/[**IV**] ≥ 10/1).

## DISCUSSION

In our opinion, the formation of radicals **I** and **III** can be explained on the assumption that the structure of the activated silica surface is responsible for the interaction of its intrinsic (diamagnetic) defects (such as oxygen vacancies ($\equiv Si\cdot\cdot Si\equiv$), which are well known as bulk defects in vitreous silica [8]) with nitromethane molecules.

The amount of nitromethane added to an Aerosil sample in our experiments was much greater than the amount of modified paramagnetic defects. During nitromethane adsorption, oxygen vacancies on the acti-

Structures and HFC constants (G) of nitroxyl radicals at 300 K

| Radical* | $a_N$ | $a_H(CH_3)$ | $a_H(\alpha\text{-}CH_2)$ | References |
|---|---|---|---|---|
| $\equiv SiOCH_2N(O^{\bullet})CH_3$ (**I**) | 12 | 11 | 5 | ** |
| $\equiv SiOCH_2ON(O^{\bullet})CH_3$ (**II**) | 30 | 8 | – | ** |
| $\equiv SiOCH_2CH_2N(O^{\bullet})CH_3$ (**III**) | 15 | 9 | 13 | ** |
| $\equiv SiOCH_2CH_2N(O^{\bullet})CD_3$ | 15 | ≤2 ($a_D(CD_3)$) | 13 | ** |
| $\equiv SiOCH_2CH_2ON(O^{\bullet})CH_3$ (**IV**) | 31 | 8 | – | ** |
| $\equiv SiON(O^{\bullet})CH_3$ | 31.5 | 7.2 | – | [6] |
| $RN(O^{\bullet})CH_3$ (R = H, $CH_3$, $C(CH_3)_3$) | 12–17 | 12–15 | – | [11, 12] |
| $HOCH_2N(O^{\bullet})C(CH_3)_3$ | 14.2 | – | 4.8 | [13] |
| $RON(O^{\bullet})R'$ (R = $CH_3$, $CH_2CH_3$, R' = $C(CH_3)_3$) | 27–30 | – | – | [14, 15] |

* The HFC constants for radicals **I**–**IV** are given to ±1 G.

** This work.

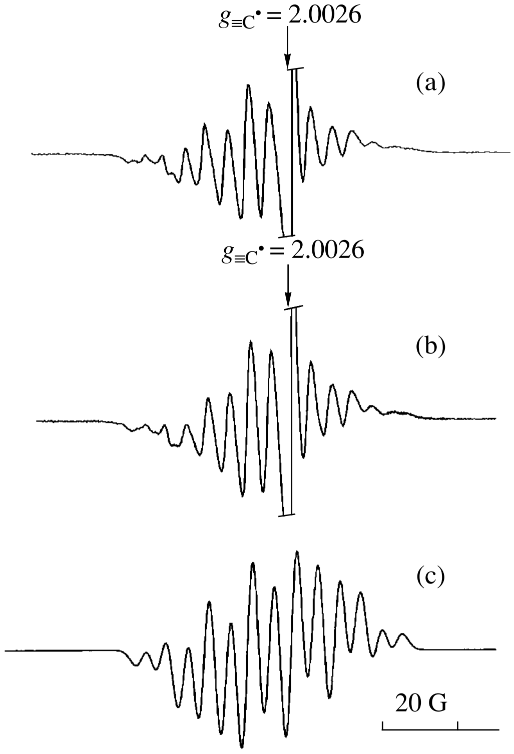
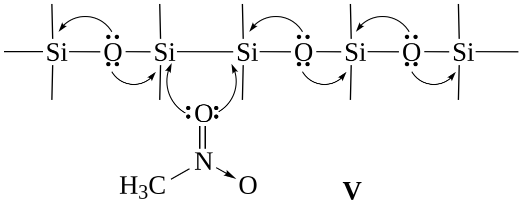


**Fig. 2.** ESR spectra of the paramagnetic reaction products of $\equiv SiOC^{\bullet}H_2$ radicals with nitromethane after holding the samples at 370 K: (a) measurement at 300 K, (b) measurement at 370 K, and (c) simulated spectrum of radical **I**.

vated silica surface can react with the lone electron pairs of an oxygen atom of the nitromethane molecule via the unoccupied 3*d* orbitals of silicon atoms (the vacant 3*d* orbitals cannot be fully occupied by the mechanism of $(p \longrightarrow d)_\pi$ conjugation with the neighboring oxygen atoms of the silicon dioxide lattice [16]). This interaction can result in the formation of diamagnetic complex **V** with the structure


**V**

If complex **V** is within reach of $\equiv SiOC^{\bullet}H_2$ or $\equiv SiOCH_2C^{\bullet}H_2$ radicals, the interaction between these radicals results in the fission of an N–O bond in the nitromethane molecule that is bound as a complex, and in the formation of corresponding radical **I** or **III** and a siloxane bond in the structure of silicon dioxide.

Thus, the following two processes can compete on the activated silica surface: the interaction of modified surface defects with complex **V**, if the latter is within reach of $\equiv SiOC^{\bullet}H_2$ or $\equiv SiOCH_2C^{\bullet}H_2$ radicals, to form the nitroxyl radicals $RN(O^{\bullet})CH_3$ (R = $\equiv SiOCH_2$ or $\equiv SiOCH_2CH_2$) and the reaction of modified paramagnetic defects directly with nitromethane molecules to form the nitroxyl radicals $RON(O^{\bullet})CH_3$.

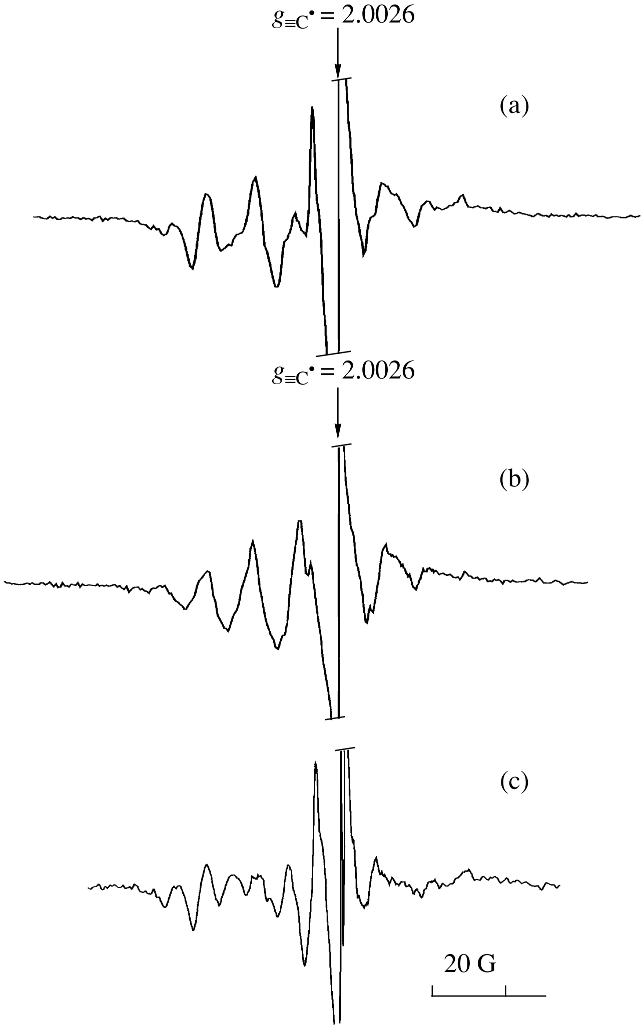


**Fig. 3.** ESR spectra of the paramagnetic reaction products of $\equiv SiOCH_2C^{\bullet}H_2$ radicals with nitromethane on RSi: (a) at 300 K, (b) after holding the sample at 370 K followed by cooling to 300 K, and (c) the result of graphical subtraction of spectra (a) and (b).

It is likely that different concentration ratios between nitroxyl radicals formed in the reaction of nitromethane with modified paramagnetic defects on the activated silica surface by different procedures can be explained as described below. In the course of activation, as the concentration of surface paramagnetic defects (on modified RSi) increased, favorable conditions were produced for the formation of additional oxygen vacancies. It is well known [17] that carbon deposits (such as carbide-like fragments, coke, or

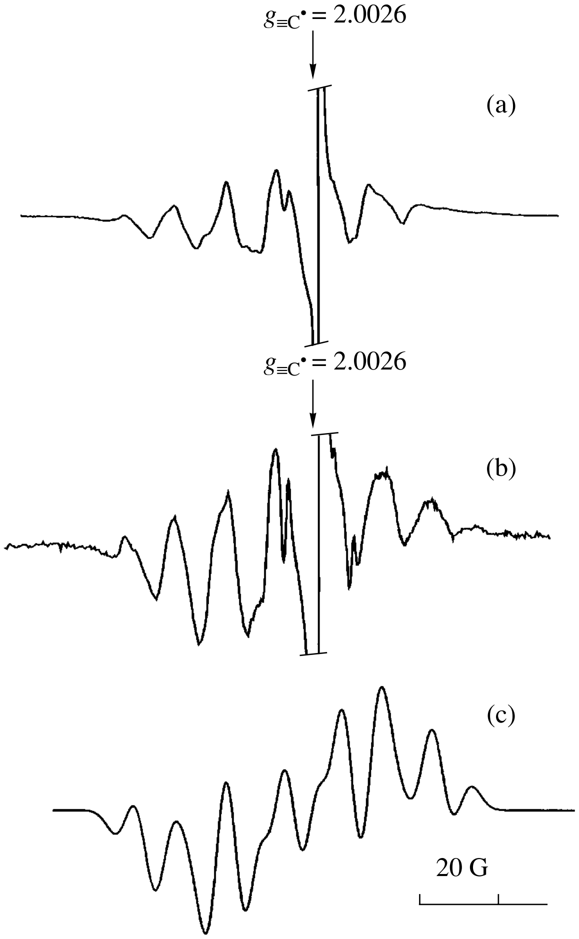


**Fig. 4.** ESR spectra of the paramagnetic reaction products of $\equiv SiOCH_2C^{\bullet}H_2$ radicals with nitromethane on modified RSi: (a) measurement at 300 K, (b) measurement at 370 K, and (c) simulated spectrum of radical **III**.

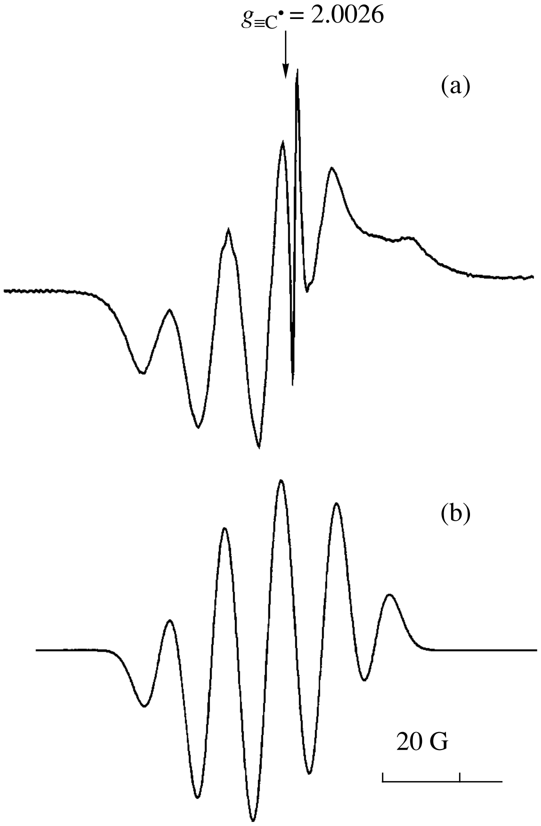


**Fig. 5.** ESR spectrum of the paramagnetic reaction product of $\equiv SiOCH_2C^{\bullet}H_2$ radicals with deuterated nitromethane on modified RSi: (a) measurement at 300 K and (b) simulated spectrum of the radical $\equiv SiOCH_2CH_2N(O^{\bullet})CD_3$.

graphite) are formed in surface layers during the thermochemical activation of Aerosil. In the course of a thermal oxidation process, the removal of carbon atoms from the surface layer can be accompanied by either the release of an additional amount of oxygen vacancies that were blocked with carbon deposits or the fission of Si–C bonds and the formation of new oxygen vacancies. In turn, this increases the probability of complexes of type **V** occurring within reach of modified paramagnetic defects and thereby facilitates the formation of the nitroxyl radicals $RN(O^{\bullet})CH_3$. Our data suggest that complex **V** almost always occurs within reach of $\equiv SiOCH_2O^{\bullet}H_2$ radicals stabilized on modified RSi; therefore, mainly one type of nitroxyl radicals are formed, namely, $\equiv SiOCH_2CH_2N(O^{\bullet})CH_3$.

Thus, nitroxyl radicals of different types are formed in the reactions of the modified paramagnetic defects $\equiv SiOC^{\bullet}H_2$ and $\equiv SiOCH_2C^{\bullet}H_2$ on the activated silica surface depending on the state of nitromethane (free or bound as complex **V**):

$$\equiv SiO(CH_2)_nC^{\bullet}H_2 + \mathbf{V}$$

$$\longrightarrow \equiv SiO(CH_2)_nCH_2N(O^{\bullet})CH_3,$$

$$\equiv SiO(CH_2)_nC^{\bullet}H_2 + CH_3NO_2$$

$$\longrightarrow \equiv SiO_2(CH_2)_nCH_2ON(O^{\bullet})CH_3 \; (n = 0, 1).$$

Previously [3], the selectivity inversion phenomenon observed in the photochemical reactions of peroxy radicals on the activated silica surface was associated with the occurrence of such diamagnetic defects. The nature of the diamagnetic defects that manifest themselves in various radical reactions on an activated surface is still an open question and calls for further investigation.

## ACKNOWLEDGMENTS

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