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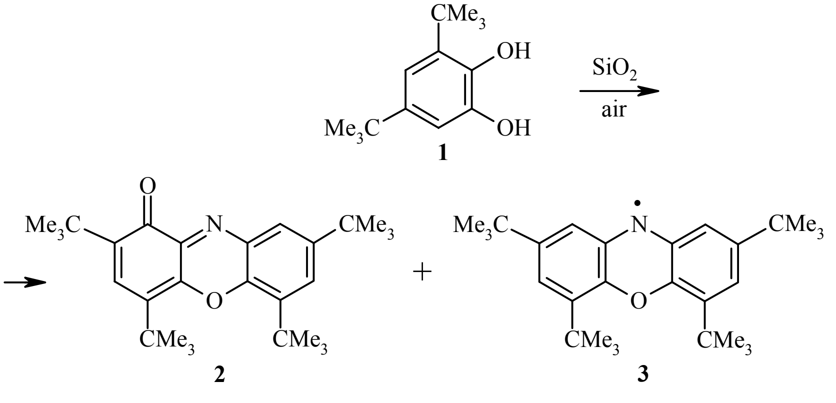
ISOTOPIC STUDY OF THE FORMATION OF PHENOXAZINE DERIVATIVES IN THE TRANSFORMATIONS OF 3,5-DI-*tert*-BUTYLCATECHOL ADSORBED IN THIN SiO_2–*n*TiO_2 LAYERS IN THE AIR

B. V. Vol'eva[1], A. I. Prokof'eva[2], N. L. Komissarova[1], I. S. Belostotskaya[1], T. I. Prokof'eva[1], and V. V. Ershov[1]

A study was carried out on the isotopic composition of the tetra-tert-butylphenoxazine derivatives formed in the heterophase transformations of 3,5-di-tert-butylcatechol adsorbed on thin SiO_2 layers with microscopic traces of Ti and Mn in a nitrogen–oxygen atmosphere enriched with $^{15}N_2$. The formation of isotopically-labeled tetra-tert-butylphenoxazinyl and hydroxytetra-tert-butylphenoxazinyl radicals and tetra-tert-butylphenoxazinone indicated the participation of atmospheric nitrogen in the heterophase catalytic reaction.

Keywords: 3,5- and 3,6-di-*tert*-butylcatechols, tetra-*tert*-butylphenoxazinyl radical, tetra-*tert*-butylphenoxazinone, SiO_2, TiO_2, heterophase transformations, reactions of atmospheric nitrogen.

In previous work [1], we discovered that 3,5-di-*tert*-butylcatechol (**1**) adsorbed on thin SiO_2 layers and exposed to the air undergoes an oxidation–reduction transformation, providing a significant amount of organic nitrogen products. 1H-2,4,6,8-Tetrakis-*tert*-butyl-1-phenoxazinone (**2**) was isolated and identified, while the 3,5,7,9-tetrakis-*tert*-butylphenoxazinyl radical (**3**) was detected by ESR spectroscopy.



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[1] N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow 117977, Russia; e-mail: ibcp@sky.chph.ras.ru, chembio@sky.chph.ras.ru. [2] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 117813, Russia. Translated from Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1145-1152, October, 2002. Original article submitted April 26, 2000.

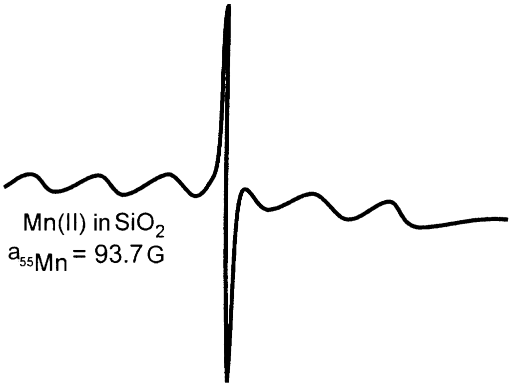
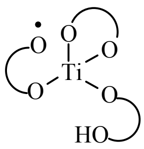
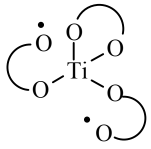


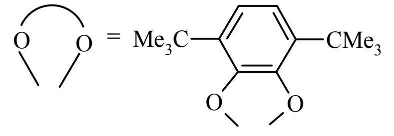
Fig. 1. ESR spectrum of microtraces of Mn(II) in SiO_2.

Catechols have been shown to be components of complex nitrogen-fixing systems capable of reducing nitrogen to N_2H_4 and NH_3 [2]. It would be natural to assume that one of the alternative sources of nitrogen for the formation of nitrogen compounds in this heterophase system might be atmospheric nitrogen. Evidence for this hypothesis was obtained in an isotopic study in a 4:1 N_2–O_2 atmosphere enriched in $^{15}N_2$ (95% enrichment). Before the isotopic experiments, we studied the reproducibility of the formation of **2** and **3** using various adsorbents such as Silufol and Kieselgel plates, SiO_2 powders, and finely ground quartz. The formation of **2** and **3** occurs only on SiO_2 samples containing microscopic traces of Ti or Ti + Mn. The presence of Mn traces as Mn^{2+} ions was recorded directly in the adsorbent (Fig. 1).

The ESR spectral parameters for Mn^{2+} compounds corresponds to the data of Saraev and Shmidt [3]. The presence of microtraces of Ti in the SiO_2 samples was also established by ESR spectroscopy using 3,6-di-*tert*-butylcatechol (**4**) as a complexone [4]. The reaction of catechol **4** with oxides of aluminum, zinc, and titanium under heterophase conditions permitted us to record free-radical *o*-semiquinone complexes of the corresponding metals. The most important finding in these experiments was the observation of the formation of mono- and diradical titanium complexes containing semiquinone ligands on the SiO_2–$n$$TiO_2$ base. In this case, satellite lines for ^{47}Ti and ^{49}Ti isotopes were observed for the monoradical complex:


(monoradical complex)


(diradical complex)



Samples of SiO_2–$n$$TiO_2$ with good reproducibility of formation of nitrogen products **2** and **3** were selected for the isotopic study. These samples were washed with methanol and degassed by prolonged evacuation at 150-160°C to eliminate impurities adsorbed on the surface. The removal of adsorbed NH_3 was especially important for our study. Thus, a rapid ESR test was developed for the detection of NH_3 involving trituration of a portion of the adsorbent with a small amount of catechol **1**. The formation of phenoxazinyl radical **3** is instantly recorded in the presence of adsorbed NH_3. This radical is not observed in purified samples. The course of the transformation of catechol **1** in an atmosphere of $^{15}N_2$–O_2 was observed visually relative to the change in color of the adsorbent. We should note that the transformation occurs much more slowly on the purified adsorbent than on samples not subjected to special treatment, probably due to change in the surface structure and the loss of groups and compounds capable of catalyzing the heterophase reaction (OH groups, H_2O, H^+, and NH_3). The strong raspberry color due to the transformation products appears only 30 days after onset of the reaction.

The isotope composition of radical **3** was analyzed by ESR spectroscopy, which permitted us to identify derivatives with ^{14}N and ^{15}N. Figure 2 shows the ESR spectra of phenoxazinyl radical **3** obtained in the transformation of catechol **1** on SiO_2–$n$$TiO_2$ in the $^{15}N_2$–O_2 gas mixture.

Analysis of the hyperfine structure of the ESR spectra shows a 1:1:1 triplet in the case of ^{14}N due to coupling of the unpaired electron with the ^{14}N nucleus ($a_{^{14}N}$ = 7.5 G). Each component of the triplet contains a triplet of triplets due to pairwise equivalent *p*- and *m*-protons to the divalent nitrogen atom (a_H^{para} = 4.12, a_H^{meta} = 2.75 G). The hyperfine coupling constants of the unpaired electron with the ring protons using the $^{15}N_2$–O_2 mixture remains invariant, while the major triplet from the ^{14}N nuclei is transformed into a doublet from the ^{15}N nucleus with spin 1/2, $a_{^{15}N}$ = 10.5 G. The ratio of the $a_{^{15}N}/a_{^{14}N}$ coupling constants (1.4) is equal to the ratio of the nuclear magnetic moments and is in accord with the NMR frequencies of these isotopes.

Thus, the ESR spectral data provide direct proof for the formation of phenoxazinyl radicals with the participation of atmospheric nitrogen.

Tetra-*tert*-butylphenoxazinone **2** formed in the isotopically labelled atmosphere was isolated by preparative thin-layer chromatography and analyzed by mass spectrometry. The molecular ion peak M^+ 422 corresponds to tetra-*tert*-butylphenoxazinone–^{15}N (Fig. 3). The molecular ion with mass 423 accompanying ion 422 corresponds to 2-hydroxy-3,5,7,9-tetrakis-*tert*-butylphenoxazinyl radical, which was confirmed by ESR spectroscopy (Fig. 4).

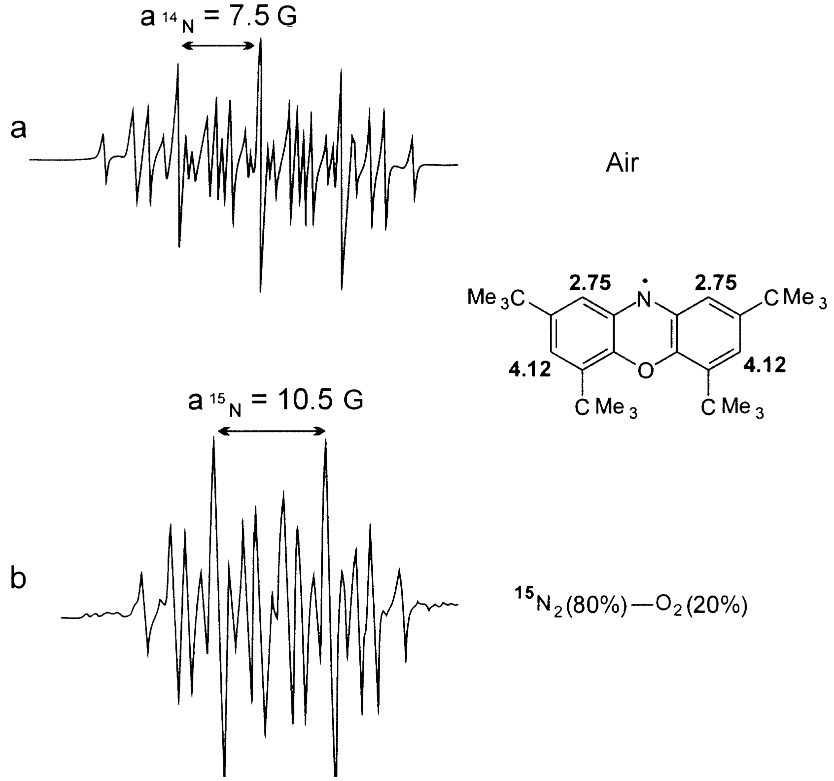


Fig. 2. ESR spectra of tetra-*tert*-butylphenoxazinyl radical **3** with ^{14}N (*a*) and ^{15}N nuclei (*b*).

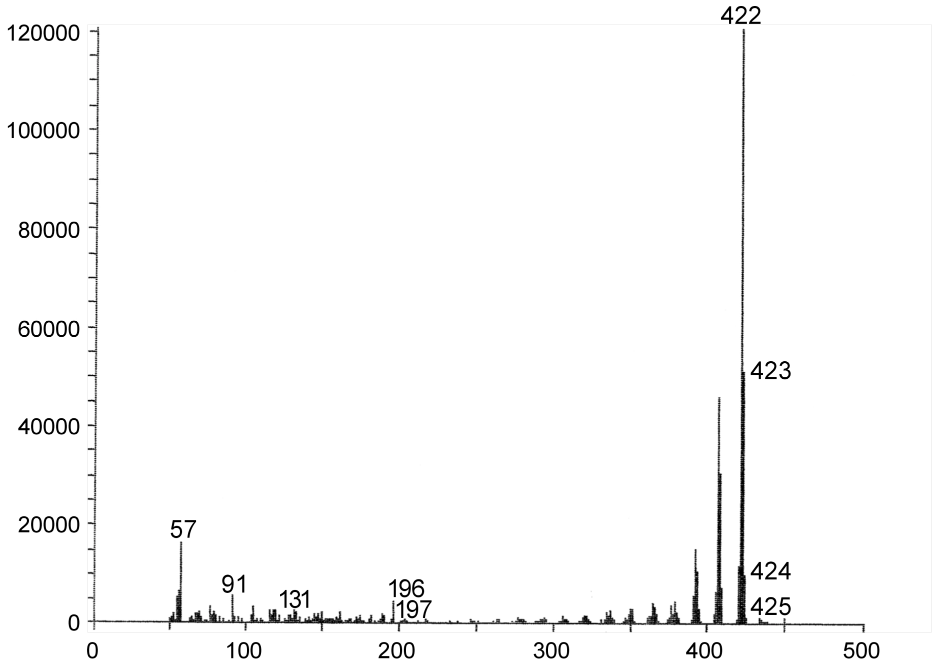


Fig. 3. Mass spectrum of tetra-*tert*-butylphenoxazinyl radical ^{15}N (M$^+$ 422) and accompanying hydroxytetra-*tert*-butylphenoxazinyl radical ^{15}N (M$^+$ 423).

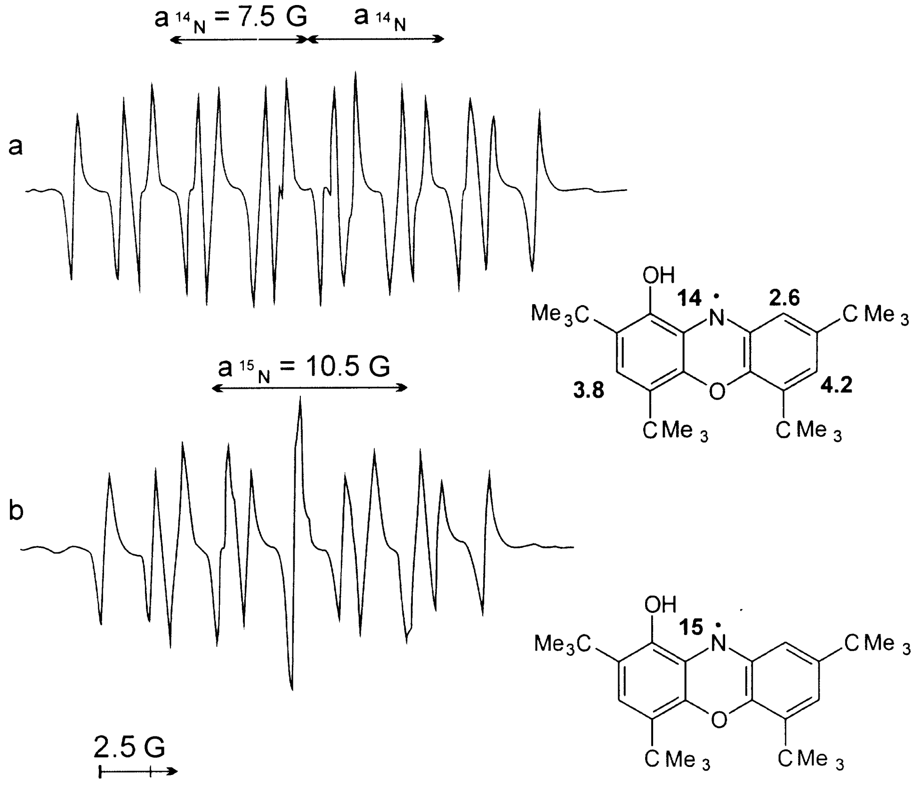


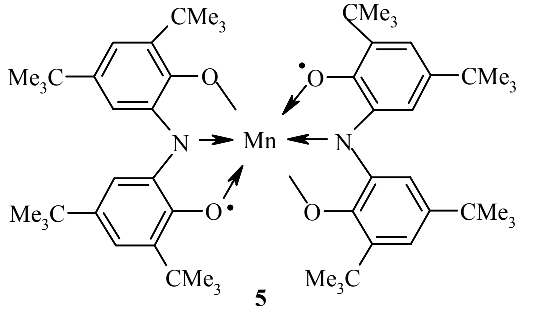
Fig. 4. ESR spectra of hydroxytetra-*tert*-butylphenoxazinyl radical with ^{14}N (*a*) and ^{15}N nuclei (*b*).

These data show that a reaction takes place in the heterophase system studied involving atmospheric nitrogen as a reagent. A definite role was also shown for traces of transition metals, which probably act as sites for realization of a coordination catalytic mechanism, in which catechol acts as an electron donor ligand, while SiO_2 acts as a structure-organizing factor permitting a multielectron mechanism for reduction of the N_2 molecule.

In the present work, we attempted to modify the catalytic system by adding inorganic compounds (TiO_2 and $Mn(OAc)_2$) and metal powders (Mo, Mn, W, V, and Co) to SiO_2. The formation of **2** and **3** is not observed on 100:1 SiO_2–TiO_2 mechanical mixtures. The excess of Ti(IV) presumably inhibits the reaction with N_2, which requires the participation of low-valence titanium ions formed in the presence of an organic reducing agent.

The major nitrogen-containing product formed on SiO_2 with added $Mn(OAc)_2$ is metal complex **5** detected by thin-layer chromatographic analysis. However, the oxidation of catechol **1** to give 3,5-di-*tert*-butyl-*o*-benzoquinone (**6**) predominates in this case. Similar behavior is found in the 100:1 SiO_2–Mn system. No formation of nitrogen compounds is found on SiO_2 with added W, Co, and V. The formation of a mixture of mono-, di-, and triligand complexes of V(III) with 3,5-di-*tert*-butyl-*ortho*-benzosemiquinolate ligands was detected on 100:1 SiO_2–V by thin-layer chromatographic analysis. These complexes are identical to the metal complexes formed in the reaction of catechol **1** and quinone **6** with V and its compounds. Triligand vanadium complex **7** was isolated preparatively and analyzed.

A weak free radical ESR signal was observed in the 100:1 SiO_2–Mo system. The spectrum of this signal corresponds to the protonated tetra-*tert*-butylphenoxazinyl radical (**8**) (see Fig. 5).



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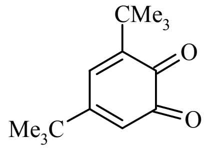

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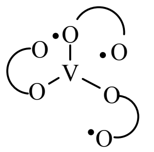

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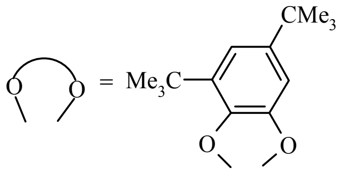

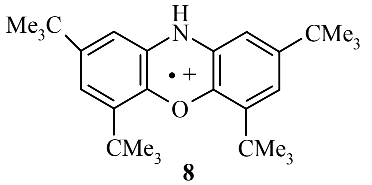

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Thus, the best results were obtained on SiO_2 with the natural content of transition metal impurities (Ti and Mn). However, the participation of atmospheric nitrogen in the heterophase transition holds undoubted interest, expanding our understanding of the reactivity of nitrogen and possible pathways for the formation of nitrogen compounds in nature.

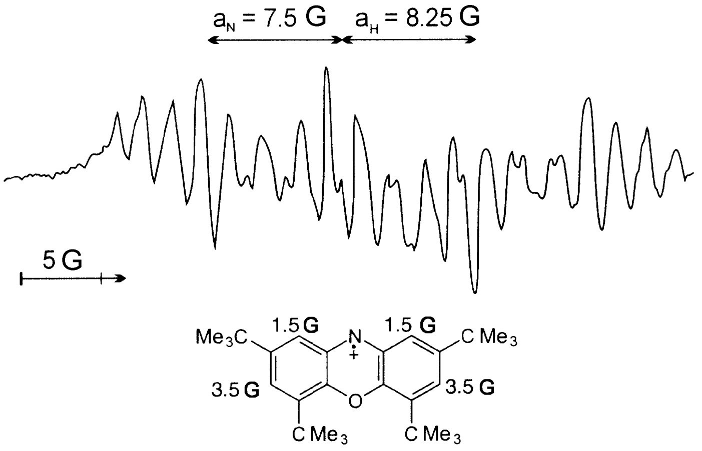

Fig. 5. ESR spectrum of protonated tetra-*tert*-butylphenoxazinyl radical.

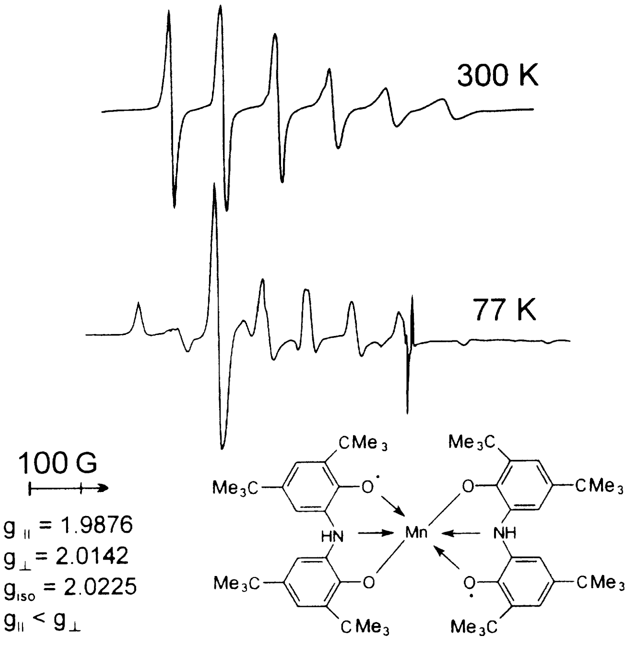

Fig. 6. ESR spectrum of Mn complex **5**.

EXPERIMENTAL

The ESR spectra were taken on a Varian E-12A spectrometer. The electron impact mass spectra were taken on a Hitachi M-80A mass spectrometer at 70 eV. Silufol UV plates with microtraces of Ti and Mn were used for the isotope experiments. Manganese was detected by ESR spectroscopy directly in the dry adsorbent (Fig. 1). The presence of microtraces of titanium were detected using catechol **4** as a complexone according to our previous procedure [4]. The plates were washed with absolute methanol and dried at 10^{-2} mm Hg for 10-12 h at 150-160°C.

A solution of 0.1 g ($5 \cdot 10^{-4}$ mol/l) catechol **1** in hexane was placed on a Silufol strip (0.05 mg reagent per cm^2 adsorbent) in a 250-ml round-bottomed flask. The flask was evacuated, filled with oxygen, and attached with a flexible connection to a glass vessel containing $^{15}N_2$ (1 g, ~800 ml) (95% enrichment determined by mass spectrometry). A strong raspberry color developed on the plate after 30 days due to transformation products of catechol **1**.

The organic compounds were extracted from the adsorbent with ether and separated by thin-layer chromatography using 5:1 hexane–ether as the eluent. The formation of tetra-*tert*-butylphenoxazinyl radical–^{15}N was detected in the raspberry fraction (Fig. 2). Hydroxytetra-*tert*-butylphenoxazinyl radical–^{15}N was detected in the blue fraction. Molecular ions with mass 422 and 423 were detected by mass spectrometry, corresponding to tetra-*tert*-butylphenoxazinone-^{15}N (Fig. 3) and its by-product, hydroxy-*tert*-butylphenoxazinone–^{15}N (Fig. 4). The adsorbents with additives were prepared by mechanical mixing in a high-speed mixer with a Z-shaped blade. The mass ratio of the adsorbent to additive (Mn, $Mn(OAc)_2$, TiO_2, Mo, V, Co, W) was 100:1. Catechol **1** was placed on glass plates with a 1-mm-thick adsorbent layer, exposed to the air, extracted with toluene, and analyzed by thin-layer chromatography and ESR spectroscopy.

SiO_2–TiO_2. No nitrogen compounds were found. The formation of quinone **6** was detected. An authentic sample of quinone **6** was obtained by the oxidation of catechol **1** with Ag_2O; mp 114-115°C (hexane) [5].

SiO_2–Mn and SiO_2–$Mn(OAc)_2$. The major reaction products are quinone **6** and metal complex **5**, detected by thin-layer chromatography versus authentic samples. Manganese complex **5** was obtained by the reaction of catechol **1** with NH_3 and $Mn(OAc)_2$ in ethanol; mp 217-218°C (ethanol, dec.). Found, %: C 74.81; H 9.35; N 3.47. $C_{56}H_{82}MnN_2O_4$. Calculated, %: C 74.58; H 9.10; N 3.17. The ESR spectrum is given in Fig. 6.

SiO_2–Co and SiO_2–W. No nitrogen compounds were found. The only reaction product detected was quinone **6**.

SiO_2–V. No nitrogen products were detected. Thin-layer chromatographic analysis indicated formation of vanadium mono-, di-, and trisemiquinone complexes.

Vanadium trisemiquinolate **7** was isolated preparatively and was found identical to a standard sample obtained by the reaction of **1** and **5** [6]. Mass spectrum: M^+ 711.

SiO_2–Mo. The formation of radical–cation **7** was detected (Fig. 5).

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