ESR study of products of transformation of 3,6-*tert*-butylpyrocatechol on alumina, zinca, silica, and titania

V. B. Vol'eva,[a] A. I. Prokof'ev,[b] A. Yu. Karmilov,[c] N. L. Komissarova,[a] I. S. Belostotskaya,[a] T. I. Prokof'eva,[a] and V. V. Ershov[a]*

[a]*N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 137 4101
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085
[c]*Institute of Synthetic Polymer Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation.
Fax: + 7 (095) 420 2229

The formation of semiquinone and phenoxazyl radicals and metallocomplexes with semiquinone ligands was observed by ESR during the interaction of di-*tert*-butylpyrocatechol with Al_2O_3, ZnO, SiO_2, and TiO_2. In the case of different modifications of SiO_2, admixtures of TiO_2 exhibit a higher reactivity in complex formation with the organic substrate.

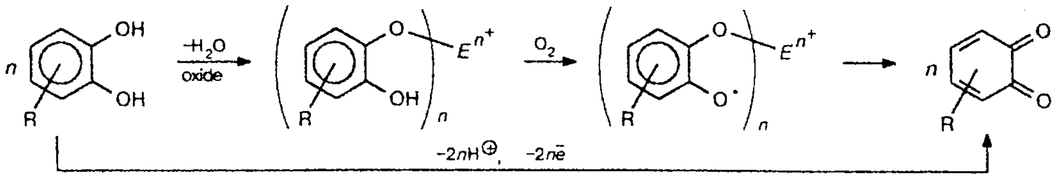
Key words: alkyl-substituted pyrocatechols; alumina, zinca, silica, titania; ESR; metallocomplexes with semiquinone ligands.

We have previously established that in thin layer chromatography (TLC), the color of spots appearing during exposure of chromatograms in air is characteristic of *tert*-butyl-substituted pyrocatechol derivatives in addition to the R_f values.[1] For example, the TLC analysis of alkylate obtained by the catalytic alkylation of pyrocatechol by isobutylene on Silufol plates in a hexane—ether (5 : 1) system of solvents showed the following sequence of elution of products coinciding with an increase in R_f: starting pyrocatechol (QH_2), 4-*tert*-butylpyrocatechol (4-BQH_2), 3-*tert*-butylpyrocatechol (3-BQH_2), 3,5-di-*tert*-butylpyrocatechol (3,5-$DBQH_2$), and 3,6-di-*tert*-butylpyrocatechol (3,6-$DBQH_2$). The colors of the spots change correspondingly: QH_2, gray; 4-BQH_2, lilac; 3-BQH_2, black; 3,5-$DBQH_2$, crimson; and 3,6-$DBQH_2$, greenish-brown. The colors are caused by the formation of complex mixtures of colored compounds during redox transformations of pyrocatechols in which the corresponding quinones and hydroquinones predominate. Nitrogen-containing organic compounds were observed among the intensely colored products of transformations of QH_2—3,5-$DBQH_2$ on SiO_2.[1]

The following paramagnetic species were detected by ESR: semiquinone and phenoxazyl radicals and metallocomplexes with semiquinone ligands. Evidently, coordination with the surface facilitates electron transfers in the pyrocatechol—semiquinone—quinone triad, and multi-electron transitions become possible (Sheme 1).

Therefore, it can be reasonably assumed that the formation of coordination compounds is one of the key stages of processes occurring on the adsorbent. We studied the products of the pyrocatechol—adsorbent interaction in more detail for the transformations of 3,6-$DBQH_2$ in thin layers of Al_2O_3, ZnO, SiO_2, and TiO_2. 3,6-$DBQH_2$ was chosen as the object for the study due to its symmetrical structure, which provided a higher stability of the metallocomplexes and simplicity of decoding ESR spectra.

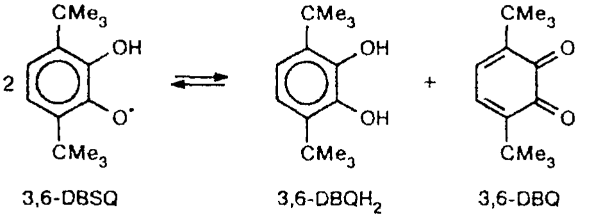
Scheme 1



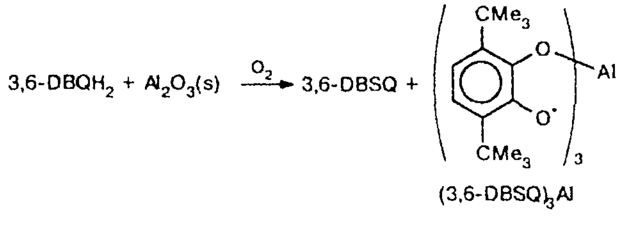
E = Al, Zn, Ti

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1975—1978, October, 1998.

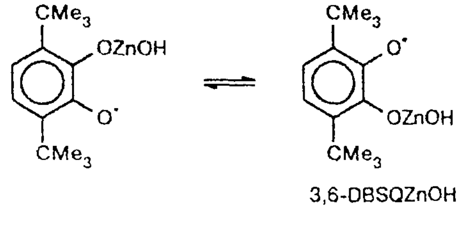
The ESR spectrum of the 3,6-DBQH$_2$—Al$_2$O$_3$ sample exposed in air for 1 day exhibits a signal, which is transformed after extraction of the sample with an organic solvent (toluene or THF) into the spectrum assigned to the semiquinone radical (3,6-DBSQ): a triplet from two equivalent protons of the ring (a_H = 3.9 Oe), each component of which is split into a doublet due to protons of the hydroxyl group (a^{OH}_H = 1.6 Oe). When the solution is frozen (77 K), the majority of semiquinone radicals disproportionates to form pyrocatechol and quinone:



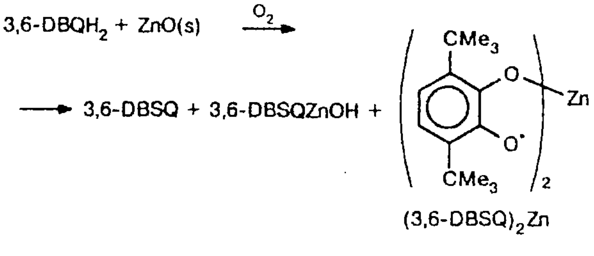
At this temperature, the ESR spectrum contains lines corresponding to the spectrum of aluminum trissemiquinolate (3,6-DBSQ)$_3$Al ($D_\perp$ = 295 Oe), which is identical to that of the compound obtained by the exchange reactions of 3,6-DBSQNa with Al^{III} salts[2] or by the solid-phase reaction of powdered Al with 3,6-DBQ under "shift-under-pressure" conditions:[3]



In the spectrum of the 3,6-DBQH$_2$—ZnO sample treated under similar conditions, signals from 3,6-DBSQ radicals and a monoradical zinc complex 3,6-DBSQZnOH (triplet from two equivalent protons, a_H = 3.3 Oe) are detected. The protons of the ring are equivalent because of the fast (in the ESR scale) migration of an unpaired electron, which is well known for coordination compounds of different elements with semiquinolate ligands:[4]



At 77 K lines of fine structure are observed, which are characteristic of triplet states or biradicals related, in this case, to zinc bis-semiquinolate (3,6-DBQ)$_2$Zn, $D_\perp$ = 210 Oe:



The ESR analysis of the 3,6-DBQH$_2$—SiO$_2$ samples after extraction with toluene established the presence of 3,6-DBSQ radicals and species, to which the doublet of doublets corresponds (a_H = 4.3 and = 3.25 Oe). The latter is characteristic of semiquinolate metallocomplexes with a low frequency of free valence migration between ligands. To identify this species, we recorded the spectra at a reduced temperature (200 K) when the equilibrium 3,6-DBSQ $\rightleftharpoons$ 3,6-DBQH$_2$ + 3,6-DBQ is shifted to the right (Fig. 1). A high amplification reveals differences between *g*-factors of 3,6-DBSQ (g = 2.0045) and metallocomplex species (g = 2.0035), and the right part

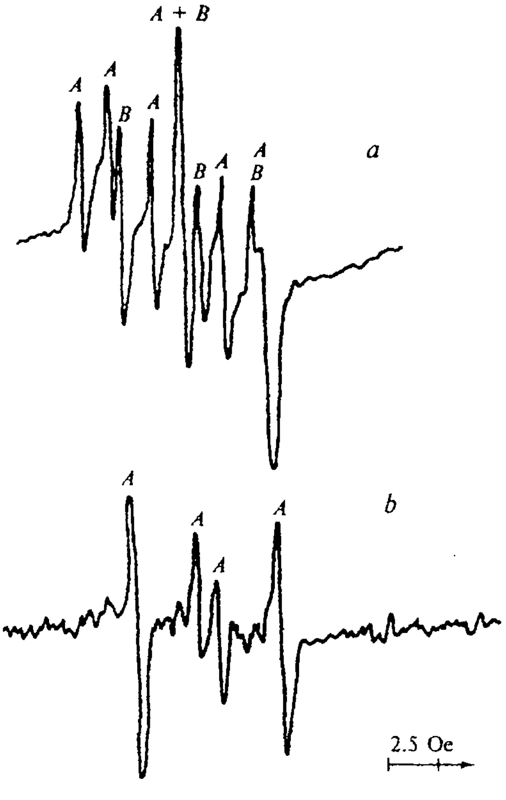


Fig. 1. ESR spectra of the 3,6-DBQH$_2$—SiO$_2$ sample extracted with toluene: *a*, superposition of spectra of 3,6-DBSQ (*A*) and 3,6-DBSQTiCatCatH (*B*) at 300 K; *b*, spectrum of 3,6-DBSQTiCatCatH (*A*) at 200 K.

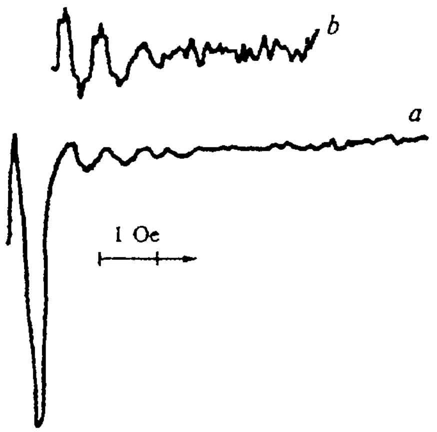


Fig. 2. *a*, Upfield edge of the spectrum of 3,6-DBSQTiCatCatH. Lines assigned to Ti^{47} and Ti^{49} isotopes (200 K); *b*, the same spectrum with a tenfold amplification.

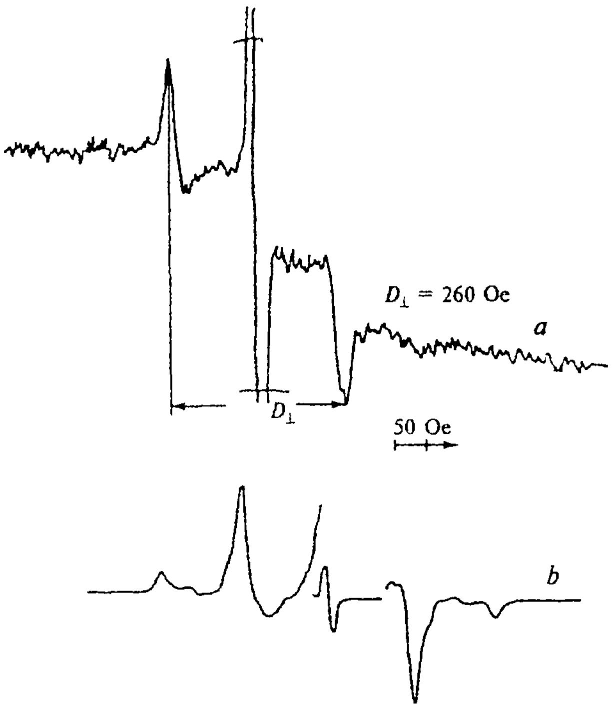
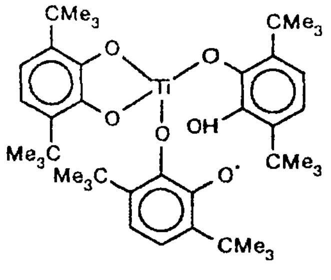
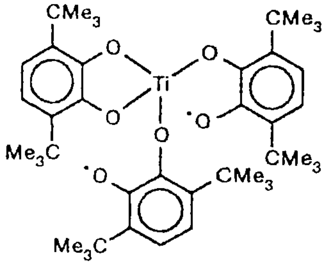


Fig. 3. ESR spectra of (3,6-DBSQ)$_2$TiCat (toluene, 77 K) on SiO_2 (*a*) and TiO_2 (*b*).

of the spectrum exhibits satellite lines (Fig. 2), whose multiplicity and intensity suggest that they correspond to titanium isotopes ($^{47}Ti_{5/2}$ 7.28% and $^{49}Ti_{7/2}$ 5.5%; $a^{47}Ti$ = $a^{49}Ti$ = 0.78 Oe). The spectrum recorded with a high amplification makes it possible to identify a paramagnetic complex corresponding to a doublet of doublets as a titanium-containing monoradical with the 3,6-DBSQTiCatCatH structure. At 77 K the spectra exhibit lines of fine structure ($D_\perp$ = 260 Oe) assigned to biradical species (3,6-DBSQ)$_2$TiCat (Fig. 3).

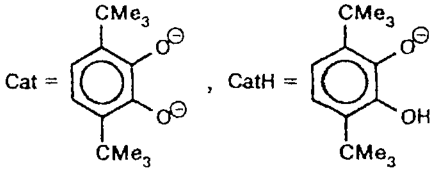


3,6-DBSQTiCatCatH



(3,6-DBSQ)$_2$TiCat,

where



The formation of similar species is typical of IV Group elements.[4]

Lines of fine structure corresponding to the (3,6-DBSQ)$_2$TiCat complex are observed directly in the 3,6-DBQH$_2$—SiO$_2$ powder.

Control experiments with the 3,6-DBQH$_2$—TiO$_2$ samples confirmed the results of identification of titanium metallocomplexes (see Fig. 3, *b*).

The spectral pattern obtained is reproduced when different modifications of SiO$_2$—Silufol, Silufol-UV$_{254}$ and UV$_{366}$, Silpearl, and Kieselgel are used. Thus, minor quantities of TiO_2 are most likely an admixture in SiO_2. The TiO_2 admixture is much more reactive in complex formation of the organic substrate than the main component SiO_2. Probably, this can be explained by localization of admixtures in defect sites with the highest reactivity.

It is noteworthy that the paramagnetic metallocomplexes detected by ESR do not include all possible structures of coordination compounds formed during the reactions of pyrocatechols with oxides. Complexes with more complicated structures (polynuclear or even network) can be catalytically active in transforming the organic substrate.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Plates with fixed Silufol, Silufol-UV_{254} and UV_{366}, Kieselgel, or Alufol layers and plates with thin layers of unfixed ZnO, TiO_2, or SiO_2 powders (thickness of the layer 0.15 mm) were used as adsorbent samples.

3,6-$DBQH_2$ was supported on plates in a hexane solution to obtain a concentration of 3,6-$DBQH_2$ from 0.05 to 0.1 mg cm^{-2}. The plates with the adsorbed substances were exposed in air for 1—3 days until an intense greenish-brown color appeared. Dry samples of substances on the adsorbent and products extracted with toluene or THF were analyzed directly by ESR. Liquid nitrogen (77 K) and an acetone—dry ice mixture (200 K) were used to cool ESR tubes.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33253a).

References

1. V. B. Vol'eva, I. S. Belostotskaya, A. Yu. Bundel', N. L. Komissarova, and V. V. Ershov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 398 [*Russ. Chem. Bull.*, 1997, **46**, 385 (Engl. Transl.)].
2. A. I. Prokof'ev, N. N. Bubnov, S. P. Solodovnikov, and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, 1979, **245**, 1123 [*Dokl. Chem.*, 1979 (Engl. Transl.)].
3. V. B. Vol'eva, A. I. Prokof'ev, V. A. Zhorin, T. I. Prokof'eva, I. S. Belostotskaya, N. L. Komissarova, A. Yu. Karmilov, and V. V. Ershov, *Khim. Fiz.*, 1996, **1**, 16 [*Russ. Chem. Phys.*, 1996, **1** (Engl. Transl.)].
4. N. N. Bubnov, S. P. Solodovnikov, A. I. Prokof'ev, and M. I. Kabachnik, *Usp. Khim.*, 1978, 1040 [*Russ. Chem. Rev.*, 1978 (Engl. Transl.)].
5. T. I. Prokof'eva, A. I. Prokof'ev, N. N. Bubnov, S. P. Solodovnikov, V. V. Ershov, and M. I. Kabachnik, *Khim. Fiz.*, 1984, **1**, 25 [*Sov. Chem. Phys.*, 1984, **1** (Engl. Transl.)].

Received November 4, 1997