Formation of high-spin complexes in reactions of oxides of the γ-Al_2O_3 type with radical pairs of sterically shielded semiquinones: a new procedure for the preparation of organometallic polyradicals and their ESR spectra

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A new simple method was developed for the preparation of organometallic bi- and triradicals by the heterogeneous reaction of γ-Al_2O_3 or analogous oxides with free radicals generated in solution through the interaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with 3,6-di-*tert*-butylpyrocatechol. An explanation was offered for the plus sign of the dipole-dipole coupling constant observed previously in the ESR spectra recorded in a superstrong field at low temperatures.

Key words: ESR spectra; oxides, organometallic polyradicals.

Polyradicals with a total electron spin $S > 1/2$ are of interest as objects for studying molecular structures, modeling organic magnetics, *etc.* There are known procedures for the generation of polyradicals based on complex processes involving metal amalgams,[1] successive replacement of anionic ligands by free-radical fragments in the corresponding salts,[2] or the mechanochemical synthesis of polyradicals.[3] In this work, we suggest a new simple procedure for the preparation of organometallic bi- and triradicals by the heterogeneous reaction of γ-Al_2O_3 (or other oxides) with free radicals generated in solution *via* the interaction of 3,6-di-*tert*-butyl-*o*-benzoquinone (DBQ) with 3,6-di-*tert*-butylpyrocatechol ($DBQH_2$):

$$(DBQ) + (DBQH_2) \rightleftharpoons 2\,(DBSQ),$$

where (DBSQ) is the corresponding 3,6-di-*tert*-butylsemiquinone radical.

Experimental

The reaction was carried out in a standard ESR tube at room temperature directly in a resonator of an ERS-220 spectrometer. α-Al_2O_3 and γ-Al_2O_3 with various specific surfaces were used. Toluene was used as the solvent. Concentrations of the complex that formed were determined relative to a $CuSO_4$ secondary standard, which was calibrated against an $Al^{3+}(DBSQ)_3$ sample with a specified concentration.

Experiments on thermal spin polarization were carried out on an ESR spectrometer (in the 2 mm range).[4] The temperature was controlled using a stream of He. A thermal accessory allowed us to carry out measurements in the range of 5—400 K.

Results and Discussion

The spectrum of a frozen toluene solution of the $Al(DBSQ)_3$ complex formed by the reaction of γ-Al_2O_3 with (DBQ) and ($DBQH_2$) is shown in Fig. 1 (spectrum *1*). The signals (spectra *2* and *3*) were observed in 1/2 H_0 and 1/3 H_0 magnetic fields (H_0 is the magnetic field for $g = 2$), *i.e.*, the complex has a spin of 3/2. The spectrum completely coincides with the signal recorded for the $Al^{3+}(DBSQ)_3$ complex synthesized according to the known procedure.[1] In addition, we used the method

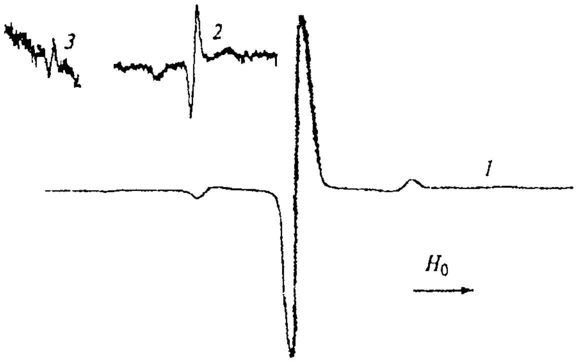

Fig. 1. ESR spectra of a vitrified solution of the $Al^{3+}(DBSQ)_3$ complex in toluene that formed in the reaction of γ-Al_2O_3 with a mixture of *o*-quinone and pyrocatechol: signals at $H = H_0$ (*1*), 1/2 H_0 (*2*), and 1/3 H_0 (*3*), respectively.

[†] Deceased.

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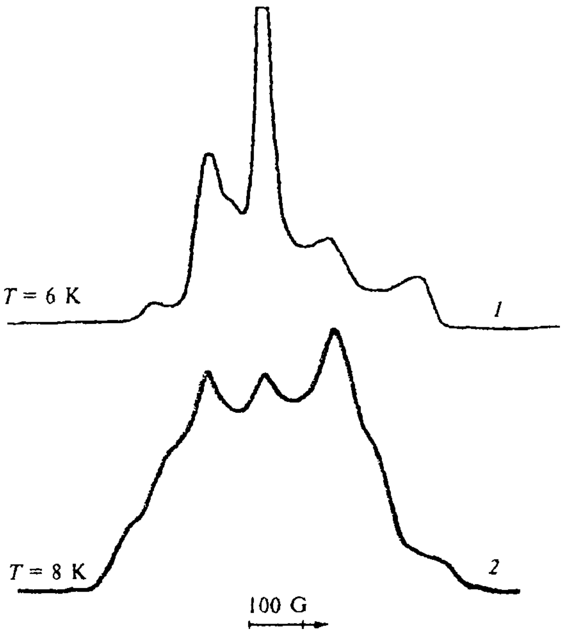


Fig. 2. ESR spectra (in the 2 mm range) under conditions of polarization of electron spins of the $Al^{3+}(DBSQ)_3$ (*1*) and $Ge^{4+}(DBSQ)_2(Cat)$ (*2*) complexes.

for observing thermal spin polarization in superstrong fields,[5] which made it possible to distinguish systems with spins $S = 1$ and $S = 3/2$. This experiment also unambiguously indicated that the system with the $S = 3/2$ occurs.

In the reactions of toluene solutions of a mixture of (DBQ) and ($DBQH_2$) with metal oxides (ZnO, GeO_2, PbO, SiO_2, MgO, or SnO_2), the $(metal)^{n+}(DBSQ)_n$ complexes form only in the case of ZnO and GeO_2. The low-temperature spectra of the $Al^{3+}(DBSQ)_3$ complex (*1*) and the $Ge^{4+}(DBSQ)_2(Cat)$ complex (*2*) (Cat is the catecholate form of 3,6-di-*tert*-butyl-*o*-benzoquinone) are shown in Fig. 2. In the spectra of the triradical complex (spectrum *1*) and the biradical complex (spectrum *2*), the polarization observed corresponds to plus and minus signs of the dipole-dipole coupling constant, respectively ($D = 276$ G for $Al^{3+}(DBSQ)_2$; and $D = -307$ G, $|E| = 34$ G for $Ge^{4+}(DBSQ)_2(Cat)$).

The parameters of the fine structure for the $Zn^{2+}(DBSQ)_2$ complex ($D = -170$ G, $|E| = 10$ G) coincide with those[2,3] for complexes prepared with the use of a metal amalgam and those obtained by a mechanochemical synthesis. For the $Ge^{4+}(DBSQ)_2(Cat)$ complex, the spectroscopic parameters are close to those reported previously[6] for complexes obtained by the reaction of bispyrocatechate with (DBQ).

We studied the dependence of the amount of the $Al^{3+}(DBSQ)_3$ complex formed on the ratio between (DBQ) and ($DBQH_2$) in a solution. It was demonstrated that the maximum amount of the complex occurs at the (DBQ) : ($DBQH_2$) ratio of 1 : 1 (Fig. 3). It is known[7] that in solution, a mixture of pyrocatechol and *o*-benzoquinone occurs in equilibrium with semiquinone radicals. Therefore, $Al^{3+}(DBSQ)_3$ was obtained in the maximum yield at the maximum concentration of semiquinone in a solution. This suggests that the initial stage of the formation of the $Al^{3+}(DBSQ)_3$ complex is the interaction of the semiquinone radical with the γ-Al_2O_3 surface. In the interaction of 100% (DBQ) with γ-Al_2O_3, the $Al^{3+}(DBSQ)_3$ complex does not evolve in the solution, and the ESR spectrum corresponds to surface-bound forms of aluminum coordinated by one or two semiquinone radicals (see below). In this case, the $Al^{3+}(DBSQ)_3$ complex forms in low yield due to the presence of an impurity of 3,6-di-*tert*-butylquinone in 3,6-di-*tert*-butylpyrocatechol, since it is known[7] that pyrocatechol is oxidized readily by atmospheric oxygen to *o*-quinone. Actually, when ($DBQH_2$) is dissolved in toluene, the ESR spectrum corresponds to that of the semiquinone radical. This radical reacts with the γ-Al_2O_3 surface to yield a small amount of the $Al^{3+}(DBSQ)_3$ complex. After learning this, we studied the reaction with the pyrocatechol : *o*-quinone ratio of 1 : 1.

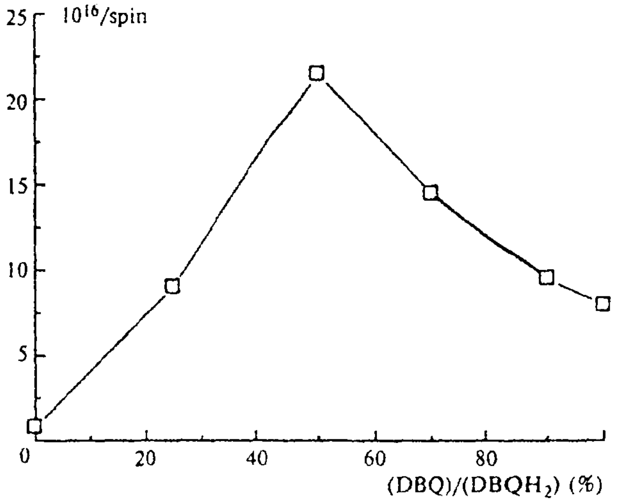


Fig. 3. Dependence of the amount of the $Al^{3+}(DBSQ)_3$ complex that formed on the ratio between (DBQ) and ($DBQH_2$) in a solution.

Another modification of aluminum oxide (α-Al_2O_3) does not react with a mixture of pyrocatechol and *o*-quinone to form $Al^{3+}(DBSQ)_3$. This is, apparently, determined by the high strength of the crystal lattice, whose structure is similar to that of silicon carbide.

The kinetics of formation of the $Al^{3+}(DBSQ)_3$ triradical was studied with the use of Al_2O_3 (2 mg) placed into an ESR tube. Then a 0.1 *M* solution of (DBQ) ($1.12 \cdot 10^{-3}$ g) and ($DBQH_2$) ($1.1 \cdot 10^{-3}$ g) in toluene was added. The intensity of the ESR signal corresponding to the $Al^{3+}(DBSQ)_3$ complex increases with time (Fig. 4, *a*). The concentration of the complex is expressed in terms of the number of spins per unit γ-Al_2O_3 surface. The initial regions of the kinetic curves

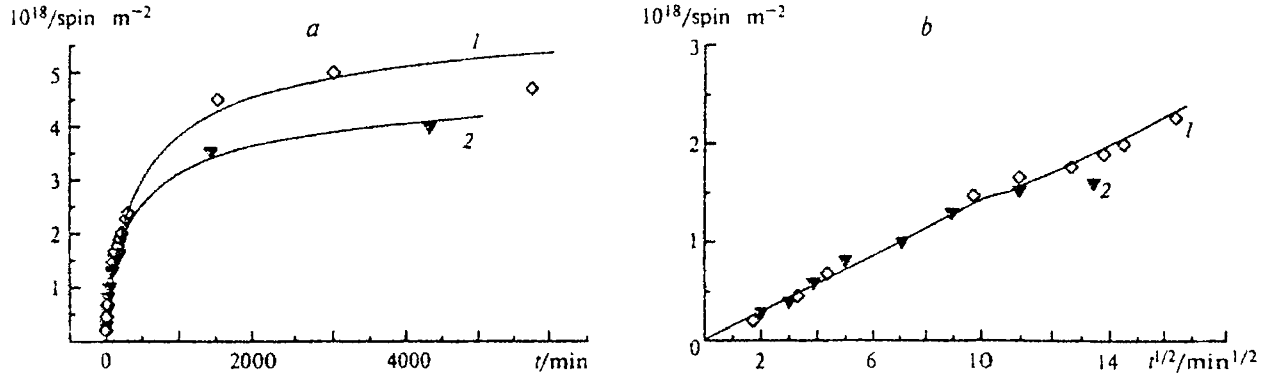


Fig. 4. *a.* Kinetic curves of the accumulation of $Al^{3+}(DBSQ)_3$; *b.* Curves of the accumulation of the $Al^{3+}(DBSQ)_3$ complex linearized on the concentration—$t^{1/2}$ coordinates (t = 120 min): *1*, Al_2O_3 with the specific surface m = 220 m^2 g^{-1}; *2*, Al_2O_3 with the specific surface m = 85 m^2 g^{-1}.

for both samples coincide. When the reactions times are large ($t > 1000$ min), the increase in the intensity of the ESR signal slows down, and the curve of accumulation of the $Al^{3+}(DBSQ)_3$ complex for a sample with a specific surface of 220 m^2 g^{-1} is somewhat higher than the curve for the sample with m = 85 m^2 g^{-1}. The initial regions of the kinetic curves are readily linearized in the coordinates of the diffusion equation ($C \sim t^{1/2}$) (see Fig. 4, *b*). This may be evidence that the reaction rate is controlled by diffusion. However, an analogous situation may also occur in the case of polychromatic kinetics[8] with a narrow distribution of reaction rates.

The decrease in the rate of formation of $Al^{3+}(DBSQ)_3$ with time may be associated with the fact that molecules of the reagents and products of the reaction block the γ-Al_2O_3 surface. To verify this suggestion, we carried out the following experiment. A γ-Al_3O_3 sample with a specific surface of 220 m^2 g^{-1} was kept with a DBQ+$DBQH_2$ mixture in a sealed tube for a month. Then the solution was decanted, and the γ-Al_2O_3 was repeatedly washed with toluene. It was established that after completion of the reaction, the γ-Al_2O_3 sample became brown, and the color remained unchanged even after careful washing with toluene. This indicates that very stable compounds of by-products of the reaction form on the surface. When a solution of a mixture of pyrocatechol and *o*-quinone was added to the γ-Al_2O_3 that had been used in the reaction and then washed with toluene, the complex did not form. This suggests that the active centers involved in forming $Al^{3+}(DBSQ)_3$ are completely blocked, and the decrease in the rate of formation of the complex with time is associated with the fact that the surface is gradually blocked. Samples of the initial oxide and samples formed after completion of the reaction were studied by X-ray structural analysis on a DRON diffractometer. In the used-up sample, the portion of the X-ray amorphous phase substantially increases, *i.e.*, in the course of the reaction, the crystal lattice is destroyed, which may be associated with the transfer of aluminum into the solution in the form of the $Al^{3+}(DBSQ)_3$ complex.

Apparently, the reaction of aluminum oxide with a mixture of *o*-quinone and pyrocatechol proceeds through several successive stages of addition of semiquinone ligands to form a triradical complex. To observe the intermediate paramagnetic particles, we carried out the following experiment. The tubes in which the reaction proceeded were placed into liquid nitrogen at certain moments. The frozen samples had signals typical of high-spin complexes, which can be identified as aluminum mono-, bi-, and triradicals formed in the course of the reaction (Fig. 5). The signal of the semiquinone radical was not observed because this radical occurs in equilibrium with an *o*-quinone+pyrocatechol mixture, and the equilibrium shifts to the initial compounds as the temperature decreases. The spectrum of the biradical exhibits typical additional splitting E (the rhombic parameter) because of the distortion of the axial symmetry of the complex. The monoradical gives a singlet at the center. At the initial stages of the reaction ($t \approx 3$ min), predominantly mono- and biradical complexes form. Increasing the reaction time ($t \approx 10$ min) increases the proportion of the triradical complex. Then the signal of the triradical becomes so high that other complexes are not observed against the background of this signal. With the aim of establishing the sites of the formation of these complexes on the surface or in the volume, the liquid fraction of the solution over Al_2O_3 was transferred into another tube and frozen, and the frozen fraction was studied by ESR spectroscopy. The spectral parameters obtained in these experiments correspond to those of the triradical aluminum complex. Even when the time of conversion was small ($t < 2$ min), spectra characteristic of mono- and biradicals were not observed. Therefore, it can be suggested that the reaction proceeds through stages of the successive addition of semiquinone ligands at the γ-Al_2O_3 surface followed by transfer of the triradical complex into the solution.

It is known[9] that a number of different centers involving OH groups, labile protons, and coordinatively unsaturated Al atoms, occurs on the γ-Al_2O_3 surface. The concentration of electron-withdrawing centers is

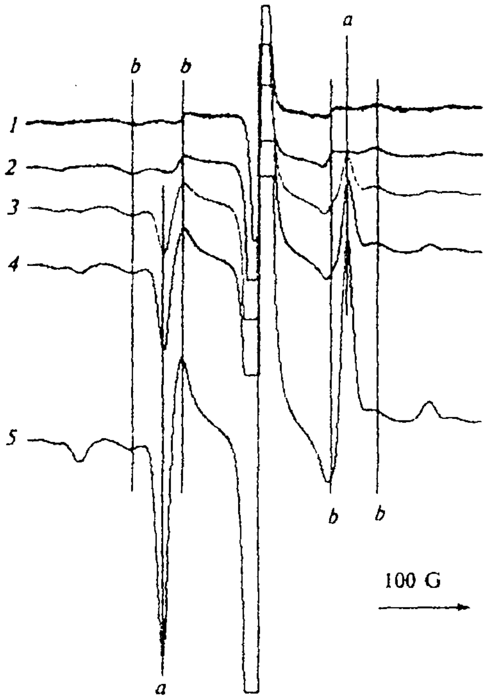
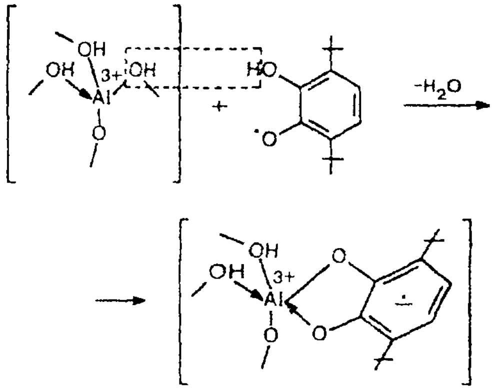


Fig. 5. ESR spectra of the reaction mixture after different times of freezing (min): 1 (*1*), 3 (*2*), 10 (*3*), 30 (*4*), and 90 (*5*). The component *a* corresponds to the triradical aluminum complex, and *b* corresponds to the biradical complex.

$\sim 2 \cdot 10^{14}$ cm^{-2}. In terms of the amount of γ-Al_2O_3 involved in the reaction (2 mg), the concentration is $9 \cdot 10^{16}$. Based on the above-mentioned data of ESR spectral studies of the used-up γ-Al_2O_3 sample, the number of blocking complexes on the surface corresponds to approximately $8 \cdot 10^{16}$ spins. This suggests that the $Al^{3+}(DBSQ)_3$ complex forms with the participation of coordinatively unsaturated Al^{3+} ions on the surface. On the other hand, when γ-Al_2O_3 is heated under a stream of nitrogen at 500 °C, the amount of the complex in solution decreases by half (t = 150 min), *i.e.*, dehydroxylation of the surface of aluminum oxide results in a decrease in the rate of formation of the $Al^{3+}(DBSQ)_3$ complex.

Elucidation of the detailed mechanism of this process calls for additional studies. A preliminary study suggests that formation of the $Al^{3+}(DBSQ)_3$ complex proceeds with the participation of the OH groups on the surface, which are highly hydroxylated under the conditions of our experiment. The reaction, which results in efficient "washout" of aluminum from the lattice, proceeds, apparently, on the surface structures with tetragonal Al^{IV}, in which the bond between aluminum and the lattice is most weakened. Previously,[10] it has been demonstrated that Al^{IV} centers coordinated by trihydroxyl groups occur. It can be suggested that triradical complexes form at these centers. As demonstrated above, a semiquinone radical is the second partner in the reaction. These radicals add at successive stages, replacing hydroxyls, cleaving bonds between aluminum atoms and the lattice, and eliminating water according to the condensation reaction. For example, the first stage may proceed according to the following scheme:



The bidentate ligand of the radical is capable of chelating an aluminum atom, which agrees with the tendency of its coordination number to increase.[11] The second and third stages of the reaction proceed analogously with an increase in the coordination of aluminum to Al^{IV}. At the final stage of addition of the third radical, the bond between the Al atom and the lattice is completely cleaved, and the complex evolves into the solution.

Therefore, in this work, we demonstrated for the first time that complexes of aluminum, zinc, and germanium can form during the interaction of their oxides with solutions of a mixture of 3,6-di-*tert*-butyl-*o*-benzoquinone and 3,6-di-*tert*-butylpyrocatechol. This is a new simple procedure for the synthesis of high-spin complexes.

We observed the formation of high-spin complexes not only in reactions proceeding in the liquid phase but also in the course of the mechanochemical treatment of a donor-acceptor mixture ($DBQ+DBQH_2$) with powdered oxide of the corresponding metal. These data allow a new interpretation of the previous results on the mechanochemical generation of high-spin compounds.[5,12] The high activity of semiquinone radicals as they form complexes with metals from oxides suggests that in some cases the radicals (formed upon trituration of powders of the initial reaction mixtures ($DBQ+DBQH_2$)) remove metals from oxides of the contacting ceramic materials used in mechanical treatment. These materials, for example, porcelain, are characterized by a high content of aluminum oxide, which may result in the formation of significant amounts of the $Al^{3+}(DBSQ)_3$ complex with spin $S = 3/2$ ($D > 0$) in addition to one- or two-spin ($D < 0$) centers. Analysis of this complex system calls for the use of a complex of radiospectroscopic methods.[13] In experiments on the effect of a shock wave pulse on the donor-acceptor mixture ($DBQ+DBQH_2$)[14] in which direct contact with ceramic materials is excluded, high-spin complexes form, whose spectroscopic parameters coincide with those of the $Al^{3+}(DBSQ)_3$ complex. The formation of these complexes is, apparently, associated with an impurity of aluminum oxide or aluminum metal in the initial compounds and in the steel anvils between which the samples were placed. The yields of high-spin compounds in the above-mentioned experiments are substantially lower than those in reactions of the donor-acceptor mixture with γ-Al_2O_3.

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