Sequential coordination of orthosemiquinone radical ligands by surface centers on γ-Al_2O_3

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The kinetics of sequential generation of mono-, bi-, and triradical centers in heterogeneous reactions of toluene solutions of orthoquinones, catechols, and their mixtures with γ-Al_2O_3 was studied. The localization of mono- and biradical centers on the solid oxide surface and the transfer of triradical $Al^{3+}(Q^{\cdot -})_3$ complexes ($Q^{\cdot -}$ is the corresponding 3,6-di-*tert*-butylsemiquinone radical) to a solution (extraction of Al from the solid phase) were proved. The number of the triradical complexes extracted is considerably higher than that of active surface centers accessible for coordination with radical ligands. The conditions favoring the formation of the radical complexes on the Al ions were established. Possible mechanisms of these processes were proposed.

Key words: ESR spectra; γ-alumina; orthoquinones, catechols, organometallic polyradicals.

It has been reported previously that the mechanical activation (grinding,[1] action of shifting pressure[2] or shock waves[3]) of solid mixtures of metallic powders and metal oxides with orthobenzoquinones (Q) and pyrocatechols (QH_2) results in the formation of stable metal complexes with quinone radicals of the $Me^{n+}(Q^{\cdot -})_n$ type. These complexes can be detected by ESR spectroscopy and identified by the characteristic fine structure (FS) of the spectra. The stable radical complexes are easily transferred to a solution without a considerable decrease in the number of paramagnetic centers. For example, in the $[\gamma\text{-}Al_2O_3+Q+QH_2]_{act}$—toluene system (index "act" corresponds to the mechanical activation of the mixture), after filtration of the solution, the spectrum of the liquid phase exhibits the signal of the $Al^{3+}(Q^{\cdot -})_3$ complex (for the registration of the FS in the ESR spectrum, the solution was frozen to exclude rotational relaxation in the complexes). However, it was observed that the $Al^{3+}(Q^{\cdot -})_3$ complexes can be formed due to the contact of the powder of γ-Al_2O_3 with a solution of the $Q+QH_2$ mixture in toluene (and without the mechanical pretreatment) rather than due to the mechanical activation of the $[\gamma\text{-}Al_2O_3+Q+QH_2]$ mixture. It was of interest to compare the mechanism of this process with the mechanism of mechanical generation of paramagnetic complexes. The reaction of "extraction" of Al from the solid matrix characterized by strong bonds occurs under mild conditions and is very unusual; therefore, its mechanism is of interest.

The preliminary results of studying this process showed[4] that mono- and biradical centers (characterized by FS different from that observed in the spectrum of the triradical) are formed being localized on the solid surface along with the soluble triradical form $Al^{3+}(Q^{\cdot -})_3$. The yield of the triradical depends substantially on the $Q : QH_2$ ratio in the solution and is the highest for a 1 : 1 composition of the mixture. This suggests that semiquinone radicals formed in the solution according to the equation

$$Q + QH_2 \rightleftharpoons 2\,Q^{\cdot}H. \qquad (1)$$

can participate in the process.

In this work, we present the results of the further study of the $[\gamma\text{-}Al_2O_3+Q+QH_2]$—toluene system. The kinetic regularities of formation of three forms of radical centers and the effect of the composition of reagents in the liquid phase and the state of the oxide surface were studied. The purpose of this work was to determine the nature of the centers involved in particular stages of the process and to establish probable mechanisms of these stages.

Experimental

γ-Alumina (A-64 trade mark, S_{sp} = 220 m^2 g^{-1}), 3,6-di-*tert*-butyl-*o*-quinone, and 3,6-di-*tert*-butylcatechol additionally purified by recrystallization were used.

The reaction was carried out in standard ESR ampoules at room temperature; after a certain time interval upon mixing the reagents, the sample was frozen in liquid nitrogen and transferred to the cavity of an ESR-220 spectrometer. The main measurements were carried out for 0.1 *M* toluene solutions of

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Q (50 μL), QH_2 (50 μL), and a $Q+QH_2$ mixture in which the concentration of each component was 0.05 mol L^{-1} (the choice of concentrations is discussed below). The standard amount of oxide in the reactor was 2 mg, which corresponds to the surface area of 0.44 m^2. In experiments with dehydrated γ-Al_2O_3, the oxide powder was subjected to thermovacuum treatment at 500 °C (10^{-3} Torr) for 3 h, then the solutions and oxide were transferred into a tube without contact with air, and the mixture was stored at room temperature and frozen as described above.

For the determination of concentrations of mono-, bi-, and triradicals, double integrals of the ESR spectra were compared to analogous characteristics of the spectra of standard samples with a known number of spins. The values obtained were corrected to take into account different spin magnitudes of the polyradical centers and the standard.[5] The amplitude of the characteristic component (Fig. 1) was measured in the spectrum, which represented the number of centers of a given type. This calibration was used further to determine the number of centers in all experimental series by the direct measurement of amplitudes in the spectra. The accuracy of relative measurements (comparison of amplitudes) was 1%; however, the accuracy of determination of absolute concentrations was lower: 10% for monoradicals and 30% for bi- and triradicals, since in the latter case, errors of double integration increase because of the considerable extension of the spectra.

Specific concentrations of active mono- and biradical centers (*C*) and rates of transformations were referred to the oxide unit surface area and expressed through the number of centers (center m^{-2} and center m^{-2} s^{-1}, respectively). This normalization procedure was used for the triradical, which is generated on the surface, although it exists in the bulk solution.

Fig. 1. ESR spectra of semiquinone radical complexes with aluminum atoms: *a*, monoradical; *b*, biradical; and *c*, triradical. Arrows mark amplitudes for calibration and measurements of concentrations (see text).

Results and Discussion

The data on the initial rates and limiting concentrations of accumulation of products in the reactions of formation of mono-, bi-, and triradicals during the interaction of hydrated and dehydrated γ-Al_2O_3 with solutions of the $Q+QH_2$ mixture and individual Q and QH_2 are presented in Table 1. Thus, six variants of the starting compositions are presented. Let us compare these results.

Table 1. Initial rates of formation (dC/dt) and limiting concentrations (C_{lim}) of mono-, bi, and triradical centers in the interaction of γ-Al_2O_3 with orthoquinones and pyrocatechols

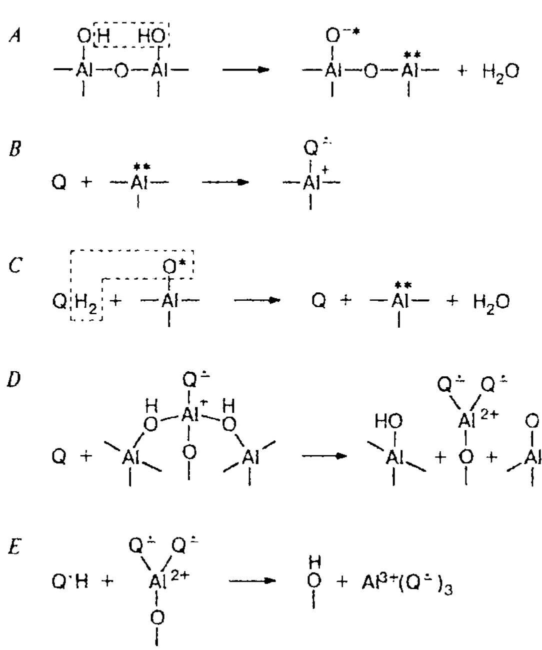
Reagents	Monoradical		Biradical		Triradical	
	dC/dt /center m^{-2} s^{-1}	C_{lim} /center m^{-2}	dC/dt /center m^{-2} s^{-1}	C_{lim} /center m^{-2}	dC/dt /center m^{-2} s^{-1}	C_{lim} /center m^{-2}
			Hydrated γ-Al_2O_3			
$Q+QH_2$	$\sim 10^{14}$	—[a]	$3.6 \cdot 10^{13}$	$3.5 \cdot 10^{16}$	$2.0 \cdot 10^{13}$	$2 \cdot 10^{18}$
QH_2	$0.5 \cdot 10^{14}$	$2.0 \cdot 10^{16}$	$2.6 \cdot 10^{13}$	$3.5 \cdot 10^{16}$	—	$<5.0 \cdot 10^{14}$ [b]
Q	$0.8 \cdot 10^{14}$	$2.2 \cdot 10^{16}$	$1.6 \cdot 10^{13}$	$3.5 \cdot 10^{16}$	—	$<5.0 \cdot 10^{14}$ [b]
			Dehydrated γ-Al_2O_3			
$Q+QH_2$	$3.8 \cdot 10^{14}$	$2.5 \cdot 10^{17}$	—	$<10^{15}$ [b]	—	$<5.0 \cdot 10^{14}$ [b]
QH_2	$1.0 \cdot 10^{14}$	$1.4 \cdot 10^{17}$	—	$<10^{15}$ [b]	—	$<5.0 \cdot 10^{14}$ [b]
Q	$2.3 \cdot 10^{14}$	$1.4 \cdot 10^{17}$	—	$<10^{15}$ [b]	—	$<5.0 \cdot 10^{14}$ [b]

[a] The spectrum is not observed because of overlapping with the spectrum of the triradical.

[b] The value corresponds to the lowest detected number of the centers, and no spectra of the radical centers are observed in this case.

A change in the state of the oxide surface has the highest effect on the processes: the dehydration of the surface suppresses the formation of bi- and triradical products to a level lower than the detection limits ($<10^{15}$ and $<5 \cdot 10^{14}$ center m^{-2}, respectively). The accumulation of monoradicals in the systems with individual solutions of Q or QH_2 occurs to equal limiting concentrations of $1.4 \cdot 10^{17}$ center m^{-2}, although the initial rate of accumulation for Q ($2.3 \cdot 10^{14}$ center m^{-2} s^{-1}) is higher than that for QH_2 (10^{14} center m^{-2} s^{-1}). When the concentrations of the initial solutions are lower than 0.1 mol L^{-1}, the initial rates and limits of accumulation of monoradicals are proportional to the content of Q or QH_2, whereas for more concentrated solutions (>0.1 mol L^{-1}), an increase in the content of Q or QH_2 does not lead to an increase in the limiting concentrations of the monoradical. Most likely, this limit is determined by the number of surface centers in γ-Al_2O_3, which are capable of acting as partners in the formation of the monoradical. This value agrees with the number of chemisorption centers determined previously[5] ($2.5 \cdot 10^{17}$ center m^{-2}) for several molecules (anthraquinone, fluoranyl, methylnaphthoquinone, and others). These centers are presumably vacancies of the terminal oxygen atom on coordinatively unsaturated tetragonal aluminum (Al^{IV}). They appear when the surface is dehydrated (Scheme 1, *A*, the terminal O atom and its vacancy are shown by one and two asterisks, respectively). These cationic centers have a vacant p-orbital of the three-coordinated Al atom and are strong Lewis acids capable of oxidizing an adsorbate and forming radical cations bound to the surface.[6] In our case, the reduction of quinone to the semiquinone radical anion requires the transfer of an electron to the Q molecule. The adjacent terminal O^- ion, which possesses reducing properties, can act as an electron donor. The reaction can occur also as the direct substitution of this oxygen ion by quinone with charging of these species. The choice between these mechanisms is most likely determined by the coordination unsaturation of Al^{IV} (the reaction does not occur on α-Al_2O_3 containing no tetragonal aluminum) rather than by the redox properties of the surface centers: the addition of bidentate orthoquinone makes it possible to increase the coordination number of aluminum. Thus, the choice between two alternative mechanisms can be reduced to the problem: which form of surface defects of Al^{IV}, the form bound to the O^- ion or the "open" form, is preferable? We have no data supporting one of these alternatives and prefer the first variant presented in Scheme 1, *B* only because "open" aluminum is sterically more accessible.

Scheme 1



The mechanisms considered for the formation of the surface monoradical form do not answer the following principal question: the transfer of one electron between two initially diamagnetic centers (oxide or a solution of quinone exhibit no ESR signal) generates a pair of radicals rather than one radical; however, the second partner is not manifested in the spectrum. Although this question is not discussed often, it arises in all cases of radical formation *via* the mechanism of one-electron transfer during adsorption of diamagnetic molecules on oxides.[6,7] One possible explanation of this phenomenon is the following: the radical-partner is transformed due to the transfer of a valence to the mobile and active form, perhaps with escape to the liquid phase where it recombines (which could take place in the case of substitution of the terminal O atom). Another explanation is that the second unpaired electron is localized on orbitals of the oxide surface centers, which interact with other orbitals including degenerate and delocalized orbitals. This results in strong inhomogeneity and significant relaxation broadening of the ESR lines of this center, which reduces their amplitude to a level below the detection limit. These concepts allow an alternative description of the process: despite the absence of the ESR signal of the starting oxide, the centers of "open" aluminum already have a nonbalanced electron spin (the full or the partial electron spin transfer from the adjacent anionic center), which does not appear due to the reason presented above. The addition of quinone is accompanied by the transfer of this electron to the molecular orbital of quinone to form the semiquinone radical observed. This process can be considered as the "manifestation" of the hidden unpaired spin of surface centers. The available data do not allow us to choose between the two mechanisms under discussion; therefore, we do not specify the electron state of surface centers in Scheme 1 (see reactions *A*—*C*) and only show them by asterisks.

According to Scheme 1, the same number of centers containing terminal oxygen atoms is formed during dehydration along with oxygen vacancies. It can be assumed that in the reaction with QH_2, protons of catechol and this O atom are preliminarily detached to form water and quinone (Scheme 1, reaction *C*). The preliminary stage of water condensation retards somewhat the reaction rate as compared to that of the direct addition of quinone, and the limiting concentrations of radicals are close in both cases.

The action of mixed solutions of $Q+QH_2$ on the dehydrated aluminum oxide results in an approximately twofold increase in the limiting concentration of the monoradical. This agrees with reactions *B* and *C* in Scheme 1, where the transformations of quinone and catechol involve the centers containing the terminal oxygen atom and its vacancies (see O* and Al** in Scheme 1, respectively), the overall concentration of which is twice that of each particular partner. It is noteworthy that the wings of the ESR line of the monoradical detected in the spectrum of the mixed system are noticeably broadened as compared to the line of the systems with individual solutions. Most likely, in this case, dipole broadening takes place, which reflects the closeness of localization of the radicals, which are coordinated on the paired centers formed during the associative desorption of water according to Scheme 1, *A*. At the same time, this dense distribution of the radicals is quite discernible from the biradical centers. The latter are characterized by a considerably higher energy of dipole-dipole interaction (greater convergence in pair) and possess a distinct ESR fine structure (see Fig. 1, *b*), *i.e.*, a regular geometry, which indicates the coordination of both radicals of the dimer on the same surface Al center. An additional confirmation of this structure of the center is given by the identity of its ESR spectrum and the spectrum of the frozen solution of the $Al^{3+}(Q^{\cdot -})_2Q^{2-}$ biradical anion obtained by the partial reduction of the $Al^{3+}(Q^{\cdot -})_3$ triradical on a Na mirror in THF.

The initial rate and accumulation limit of the monoradical decrease by an order of magnitude on going from the dehydrated oxide surface to the hydrated surface in the reaction with solutions of Q and QH_2 (see Table 1). It is difficult to determine the kinetic parameters of formation of the monoradicals on the hydrated samples in the reactions with a solution of $Q+QH_2$, because the triradical complexes are also formed in this case, and for them the ESR line of the transitions $M_S = -1/2 \leftrightarrow 1/2$ in the spin quartet and doublets is superimposed on the line of the monoradical. The estimations from the spectra at the early stage of accumulation, when the number of triradicals is still low, show that under these conditions, the yield of the monoradical is approximately an order of magnitude lower than that in the reactions with the dehydrated surface. This correlates with the decrease in the number of the aforementioned surface centers of chemisorption to 10^{16} center m^{-2}, which was determined by other methods.[5] However, in addition to monoradicals, biradical centers are also formed and stabilized on the hydrated surface, the initial rate of their accumulation being close to that for the monoradicals, and the limiting concentration is even higher. The total number of mono- and biradical centers determined for the hydrated surface becomes comparable with the number of monoradicals on the dehydrated surface, which was compared above to the number of "open" Al^{IV} atoms. Thus, a certain number of surface centers of tetragonal aluminum on hydrated oxide can coordinate a pair of semiquinone radicals; however, it loses this pair during dehydration.

This modification of the properties can be explained as follows. When the biradical center is formed, the coordination of the second semiquinone radical on the Al atom cannot occur by the simple addition of quinone from the solution, as this occurs during the formation of the monoradical. To provide an additional free valence of the Al atom, one should cleave one or more bonds of aluminum with adjacent oxygen atoms of the lattice, which makes it also possible to "raise" a little the Al atom above the surface and eliminate steric hindrances for the arrangement of two bulky ligands. It can be assumed that bonds with lateral oxygen atoms of surface Al—O—Al bridges undergo cleavage. In the case of the hydrated oxide surface, these O atoms are predominantly present as Al—OH—Al fragments, which weakens the Al—O bonds and favors their cleavage during the addition of quinone (see Scheme 1, reaction *D*). As for reactions *A* and *B*, we do not specify here the spin and charge states of the surface centers of the nearest environment of the biradical. These bridged fragments lose a proton during the thermovacuum treatment, which prevents bond cleavage and addition of a second quinone molecule: the reaction ceases at the stage of formation of the monoradical surface complexes.

The formation of the triradical complex is accompanied by final cleavage of the bonds of the Al atoms with the oxide lattice and by the escape of the triradical in the solution. This stage takes place only for the interaction of the hydrated aluminum oxide with a solution of the $Q+QH_2$ mixture. Probably, at this stage, the reaction occurs with the participation of the semiquinone radical, which is present in the mixed solution according to Eq. (1).

If the initial rate of accumulation of the triradical in the solution is determined by the number of transformations referred to the unit of surface area (for comparison with the rates of formation of the mono- and biradical centers), this value is equal to $2 \cdot 10^{13}$ center m^{-2} s^{-1}, which is somewhat lower than the rate of formation of the surface mono- and biradical centers at the preceding stages of the process. However, the increase in the triradical concentration in the solution occurs in parallel with a continuous decrease in the rate at the reaction duration up to 20 days when the number of triradicals in the bulk solution reaches 10^{18} centers. When referred to a unit of surface area, this value corresponds to $2 \cdot 10^{18}$ center m^{-2}, which exceeds substantially the number of surface centers linked to the tetragonally coordinated Al atoms and determined from the limiting number of radicals and other species adsorbed or formed on the γ-Al_2O_3 surface.[5] Evidently, "extraction" of aluminum opens new centers on the surface, which are capable of coordinating quinones in the series of transformations described followed by escape of additional Al atoms into the solution in the form of triradical complexes (see Scheme 1, *E*). This etching of the surface of the very stable compound, which is often used as a catalyst (*i.e.*, an unconsumed substrate) in processes occurring under much more severe conditions, is of undoubted interest for chemists.

The system considered is characterized by the interaction of the reagents with flexible properties. It is known[8] that one-electron transitions between the states occur readily:

$$Q \underset{-e}{\overset{+e}{\rightleftharpoons}} Q^{\cdot -} \underset{-e}{\overset{+e}{\rightleftharpoons}} Q^{2-}.$$

Quinone Semiquinone Catechol

At the same time, centers of different nature, which can adsorb molecules *via* the mechanism that involves withdrawing or donating one or two electrons, can be present on the γ-Al_2O_3 surface, and the electron structure of these adsorption centers is also labile: the bond redistribution and a change in conformation and coordination number of the metal can take place in this structure. The chelate structure of a pair of carbonyl O atoms in orthoquinones determines the possibility of their bidentate coordination, so that in a series of sequential stages of addition to the coordinatively unsaturated tetragonal Al atom, its coordination number increases and reaches 6 in the triradical complex. At the stages when the Al atom "switches" from bonds with bridging O atoms of oxide to bonds with ligands, protons localized on these oxygen atoms play a special role.

The multistage scheme of the process with optimization of each stage due to the rearrangement and compensation of bonds and charges provides an unexpectedly high efficiency of the process. In this case, the analogy with several processes in the living nature is acceptable. For example, electron transfer chains in photosynthetic centers include, along with other compounds, the same elements (quinones, metals, *etc.*), and functioning of the transport chains is determined by the lability of the geometric and electron structure of the elements, which allows one to optimize each stage of the process. It is of interest to mention the analogy with the related group of reactions observed in mechanically activated solid mixtures of quinones with metal oxides.[3] As mentioned above, these transformations, which occur under substantially nonequilibrium conditions, result in the formation of the same products (complexes of semiquinone radicals with metal ions), and in this case, low-coordinated complexes are linked to the oxide surface, and high-coordinated complexes are removed from the surface. For mechanochemical reactions, it is very difficult to study intermediate stages, since primary processes occur directly during the action and they are not usually observed, whereas the products are aggregated, as a rule, which prevents their spectroscopic analysis. In this respect, the detailed study of the processes occurring during the reaction of these reagents under the mild conditions of the oxide—solution system makes it possible to speculate on the possible mechanisms of mechanochemical reactions.

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