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# Redox Transformations and Antiradical Activity of Triarylantimony(V) 3,6-Di-*tert*-butyl-4,5-dimethoxycatecholates

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**Abstract**—Triarylantimony(V) catecholate complexes were synthesized by the oxidative addition of 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzoquinone to triarylstibines. The electrochemical properties and antiradical activity of the synthesized compounds were studied. According to cyclic viltammetry data, the complexes are oxidized via two consecutive quasi-reversible stages. Introduction of halogen atoms in *para*-position of phenyl groups at Sb(V) causes anodic shifts of the oxidation potentials and enhances stability of the mono- and dicationic forms of the compounds, which form in the course of electrochemical transformations. Triarylantimony(V) catecholate complexes exhibit appreciable antiradical activity in the auto-oxidation of oleic acid. In was found that the inhibitory activity of the complexes depends on their redox potential.

**Keywords:** organometallic compounds, antimony(V) catecholates, redox-active ligands, electrochemistry, antiradical activity

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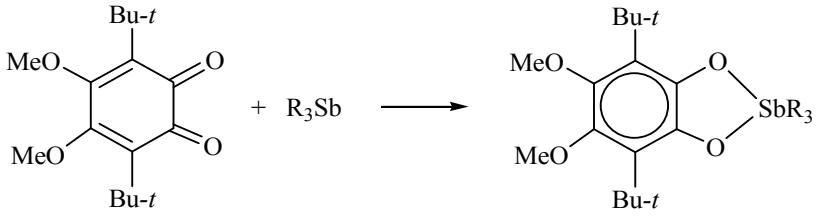
Previously we showed that the redox characteristics, antiradical activity of organo-antimony(V) complexes with redox-active ligands, as well as their ability to bind molecular oxygen depends on a variety of factors [1–6]. Electron-donating substituent group in the redox-active fragment facilitates $O_2$ binding, shifts anodic oxidation potentials to the cathodic region, and enhances the antiradical activity of Sb(V) compounds [7, 8]. Electron withdrawing groups in the catecholate ligand increase the potentials of the catecholate–*o*-semiquinolate–*o*-benzoquinone redox transitions and sometimes alter the mechanism of electrochemical oxidation of triphenylantimony(V) catecholate complexes from a two-stage one-electron transfer to one-stage two-electron transfer process [9, 10]. The stability of the cationic complexes resulting from electrochemical oxidation is also affected by the nature of the heteroatoms forming five-membered N,O-, O,O- or S,S-metallocycles [11–14]. The properties of Sb(V) catecholate complexes can also be varied not only by varying substituents in the redox-active ligand, but also by functionalizing groups linked to the central antimony atom [15]. In the present work we continued to study the effect of aryl substituents (phenyl, *p*-chlorophenyl, *p*-fluorophenyl) in the organometallic fragment $SbR_3$ of triarylantimony(V) 3,6-di-*tert*-butyl-4,5-dimethoxycatecholate complexes on the electrochemical transformations and antiradical activity in the auto-oxidation of oleic acid.

We have synthesized triphenylantimony, tri-*p*-chlorophenyl-, and tri-*p*-chlorophenylantimony catecholate complexes **I–III** by the oxidative addition of the corresponding triarylstibines to 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzoquinone (Scheme 1).

Complex **I** was described in [5]. Complexes **II** and **III** were characterized by $^1H$ and $^{13}C$ NMR spectroscopy and mass spectrometry; their structure was found to be consistent with the suggested formulas. The oxidation potential relates to the reducing ability of a compound and is a factor which allows one to predict the antiradical activity. The electrochemical

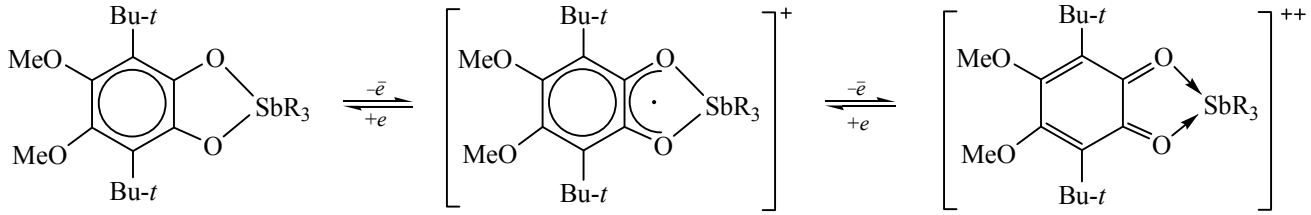
**Scheme 1.**




I–III

R = Ph (**I**), 4-$ClC_6H_4$ (**II**), 4-$FC_6H_4$ (**III**).

**Scheme 2.**




**II, III**

properties of compounds **I–III** were studied by cyclic voltammetry (CV) (see table).

The electrochemical oxidation of complexes **I–III** on a glassy carbon electrode in dichloromethane in anaerobic conditions is a two-stage process (Fig. 1). The first anodic stage is one-electron quasi-reversible process. Unlike what was previously observed with complex **I**, where the second redox process was irreversible [1], in the case of compounds **II** and **III** the second stage is a quasi-reversible process (Fig. 1). The calculated currents ratios ($I_c/I_a$) for catecholate complexes **II** and **III** are close to those for triphenylantimony *o*-amidophenolate and point to partial stabilization of the dicationic form of the complexes, which is formed in the second electrode process. Halogen substituents in complexes **II** and **III** stabilize their oxidized forms compared to complex **I**, as evidenced by the $I_c/I_a$ ratios. The observed electrochemical transformations of the complexes suggest formation of mono- and dicationic complexes with, respectively, *o*-semiquinone and *o*-benzoquinone forms of ligands (Scheme 2).

The mono- and dicationic forms of the complexes are fairly stable, but the reverse scan of the CV curve at potentials up to 0.9 V (Fig. 1, curve *1*) contains a low-intensity peak assignable to a partial decomposition product. Extending the potential sweep range to 1.5 V (Fig. 1, curve *2*) results in the appearance of

Oxidation potentials of compounds **I–IV** by cyclic voltammetry [glassy carbon electrode, $CH_2Cl_2$, $V$ = 0.2 V/s, 0.1 M $NBu_4ClO_4$, $c = 2 \times 10^{-3}$ M, Ar, Ag/AgCl/sat. KCl)][a]

| Comp. no. | $E^1_{1/2}$, V | $I_c/I_a$ | $n$ | $E^2_{1/2}$, V | $I_c/I_a$ | $E_{pa}$, V | $E_{pc}$, V |
|---|---|---|---|---|---|---|---|
| I | 0.65 | 0.75 | 1.0 | 1.08[b] | – | 1.28 | –1.26 |
| II | 0.70 | 0.94 | 1.0 | 1.12 | 0.54 | 1.56 | –1.03 |
| III | 0.68 | 0.89 | 1.0 | 1.07 | 0.45 | 1.58 | –1.00 |
| IV[c] | 0.70 | 0.90 | 1.0 | 1.14[b] | – | 1.30 | –1.09 |

[a] ($E^1_{1/2}$) Half-wave potential of the first anodic process; ($E^2_{1/2}$) Half-wave potential of the second anodic stage; ($I_c/I_a$) ration of the reverse cathodic and forward anodic currents; ($n$) number of electrons transferred in the first anodic stage, relative to ferrocene (standard); ($E_{pa}$, $E_{pc}$) oxidation and reduction peak potentials of spiroendoperoxides **V, VI**, measured in aerobic conditions. [b] Oxidation peak potentials. [c] Data from [1] for triphenylantimony(V) 3,6-di-*tert*-butyl-4-methoxycatecholate **IV**.

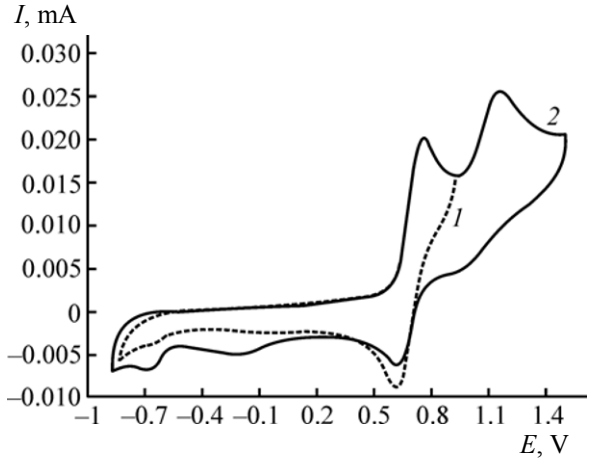



**Fig. 1.** Voltammograms of the oxidation of complex **III** in the potential sweep range from (*1*) −0.85 to 0.9 V and (*2*) from −0.85 to 1.5 V (*2*). $CH_2Cl_2$, glassy carbon anode, Ag/AgCl/KCl, 0.1 M $NBu_4ClO_4$, $c = 2 \times 10^{-3}$ M, argon.

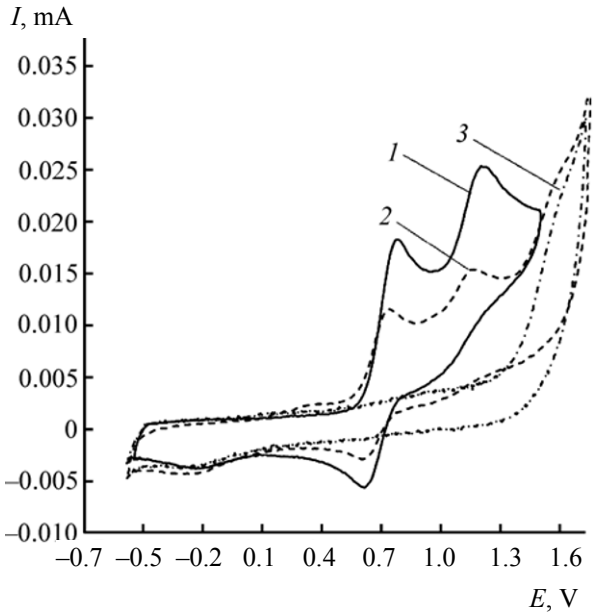



**Fig. 2.** Voltammograms of the oxidation of complex **II** in the potential sweep range from −0.60 to 1.70 V: (*1*) in anaerobic conditions (argon); (*2*) after 15 min in aerobic conditions; and (*3*) after 25 min in aerobic conditions ($CH_2Cl_2$, glassy carbon anode, Ag/AgCl/KCl, 0.1 M $NBu_4ClO_4$, $c = 2 \times 10^{-3}$ M).

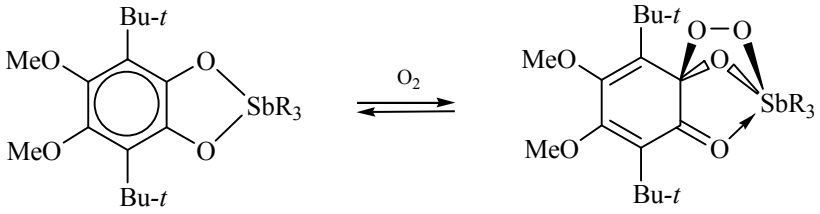
peaks of products of the chemical stage following the second electron transfer of the reverse branch of the CV curve. The increase of the cathodic current at –0.70 V is associated with decoordination of the neutral *o*-benzoquinone formed by partial decomposition of the the dicationic complex.

Halogenation of the phenyl group leads to a synchronous anodic shift of the oxidation potentials of complexes **II** and **III** for the first and second redox processes to the anodic region, and the stronger effect was observed for complex **II**. Substituion of hydrogen by chlorine in position *4* of the aromatic ring at Sb(V) has the same effect on electrochemical parameter as removal of one methoxy group from the ligand (see table).

As shown in [5, 11], complex **I** and triphenylantimony(V) *o*-amidophenolates can reversibly bind molecular oxygen. The redox potential of the catecholate/*o*-semiquinolate transformation, stability of the formed monocationic form of the complex, degree of filling of the coordination sphere of Sb(V) are among key factors controlling formation and stability of endoperoxide complexes. Catecholate complexes whose oxidation produces relatively stable radical anion forms of the ligands and whose oxidation half-wave potentials are lower than or close to 0.70 V are capable of reversibly binding oxygen [1, 7]. Cyclic voltammetry, along with NMR, is a convenient and simple method for identification of spiroendoperoxides formed on reaction with molecular oxygen [1]. Electrochemical studies showed that the oxidation half-wave potentials of compounds **II** and **III** for the first redox transition were 0.68 and 0.70 V. Consequently, it was reasonable to expect that these compounds would bind oxygen. Aeration of complexes **II** and **III** led to a change in the CV curve. Initially, the oxidation peak currents decreased, and a new anodic peak appeared (Fig. 2, curve *2*). After 25–30 min, the CV curves revealed no electrochemical activity of starting compounds **II** and **III**, but showed oxidation peaks of spiroendoperoxides at ($E^*_{pa}$) – 1.56 and – 1.58 V (Fig. 2, curve *3*).

We showed previously [1] on an example of complex **I**, that spiroendoperoxides **V** and **VI** undergo irreversible oxidation with elimination of *o*-benzoquinone [1]. When the anodic potential sweep was reversed, reduction peaks of the spiroendoperoxides appeared in the anodic region ($E^*_{pc}$), while compounds **I**–**III** showed no redox actrivity in the range from 0.0 to –2.0 V (vs. Ag/AgCl).

**Scheme 3.**




**II, III** **V, VI**

R = 4-$ClC_6H_4$ (**II, V**), 4-$FC_6H_5$ (**III, VI**).

As seen from the table, halogen substitution affects the redox parameters of not only starting complexes **II** and **III**, but also their spiroendoperoxides **V** and **VI**. The oxidation (reduction) potentials of compounds **V** and **VI** are shifted to the anodic region by 0.23–0.30 V compared to the respective parameters of the spiroendoperoxide obtained from complex **I**. Our results suggest electronic interaction between the redox-active catecholate ligand and substituents in organometallic fragment $SbR_3$, that are intervened by a nontransition metal atom (Scheme 3).

In [2, 8] we showed that triphenylantimony(V) complexes with redox-active ligands exhibit pronounced antiradical activity and revealed a reverse correlation between inhibitory activity and oxidation potential. To provide further evidence for such correlation, in the present work we studied the antiradical activity of complexes **I**–**III** and 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzoquinone in the auto-oxidation of oleic acid at 60°C. This system mimics peroxidation of biomembrane lipids. The effect was evaluated by measuring the concentration of hydroxides LOOH (primary oxidation products of oleic acid). The resulting kinetic curves are presented in Fig. 3.

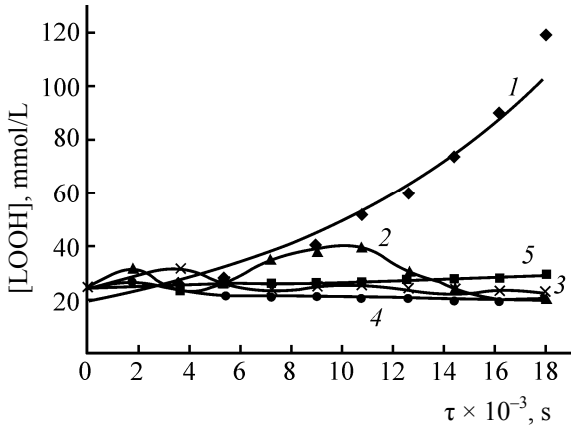


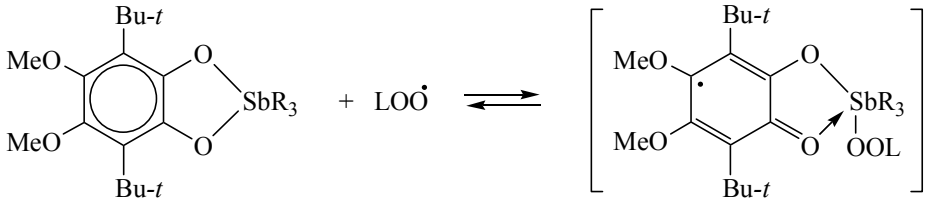

**Fig. 3.** Kinetic curves of the accumulation of LOOH during oxidation of oleic acid at 60°C (*1*) without additions and with additions (1 mM) of complexes (*2*) **I**, (*3*) **II**, and (*4*) **III**, and (*5*) 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-quinone.

Addition of complexes **I** and **II** first results in a slight increase of the concentration of hydroperoxides in the system (Fig. 3, curves *2* and *3*). In our previous work [2] we observed cyclic alterations in the concentration of LOOH: accumulation gave place to decomposition. Such alterations are caused by spiroendoperoxides formed in aerobic conditions and acting as promotors of lipid peroxidation. As the temperature is increased to 60°C, the equilibrium shifts to the starting catecholates which can react with active peroxyl radicals. In the case of complex **I**, this leads to a decrease in the concentration of peroxides, whereas with complexes **II** and **III** , an inductive period takes place (Fig. 3, curves *3* and *4*). Thus, complexes **I**–**III** exhibit antiradical activity and prevent auto-oxidation of oleic acid. The redox-active catecholate fragment endows these compounds by the ability to intercept active $LOO^{\cdot}$ radicals.

A sterically hindered *o*-benzoquinone derivative **IV** (Fig. 3, curve *5*) also inhibits the radical chain process. This effect is consistent with the known property of quinones to act as antioxidants. Pototskaya et al. [16] established in their study on the effect of phenols and quinones on the free-radical fragmentation of glycerophospholipids and their simulators that quinones are more effective inhibitors than catechols [16]. As oxidants, quinones act as selective inhibitors reacting with hydroalkylperoxyl, hydro-peroxyl, and hydroxyperoxyl radicals [17].

The inhibitory efficiency of the complexes was calculated to show that the efficiency of inhibition of oleic acid auto-oxidation correlates with their oxidation potential. The inhibitory efficiencies of complexes **II** and **IV**, whose first anodic potentials are

**Scheme 4.**




equal to each other, are 81.2 and 81.5%, respectively. The respective values for compounds **I** and **III** are 83.1 and 83.4%, respectively. 3,6-Di-*tert*-butyl-4,5-dimethoxy-*o*-benzoquinone studied in the present work is, like triphenylantimony(V) catecholate complexes, one of the most potent inhibitors of oleic acid oxidation; its inhibitory efficiency was evaluated at 75.8%.

Thus, in the present work we have synthesized novel triarylantimony(V) 3,6-di-*tert*-butyl-4,5-dimethoxycatecholate complexes, studied their electrochemical transformations, and evaluated their antiradical activity in the auto-oxidation of oleic acid. The electrochemical oxidation of complexes **II** and **III** involves two consecutive quasi-reversible stages, whereas in the case of triphenylantimony(V) catecholate (**I**) the second anodic process is irreversible. Substitution of hydrogen in position 4 of the phenyl group by chlorine or fluorine shifts the oxidation potentials to the anodic region, which relates not only to complexes **II** and **III** , but also to their spiroendoperoxides **V** and **VI** formed in aerobic conditions.

Addition of complexes **I**–**III** and 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzoquinone act to decrease the concentration of hydroperoxides during auto-oxidation of oleic acid. The antiradical activity of the complexes is explained by the reaction of the redox-active catecholate fragment with active $LOO^{\cdot}$ radicals (Scheme 4). The inhibitory efficiency of the compounds was found to correlate with their oxidation potentials. The results of electrochemical and antiradical activity studies provide evidence for electronic interaction between the redox-active catecholate ligand and substituents at the Sb(V) atom.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were measured on a Bruker AVANCE DPX-200 spectrometer relative to TMS, solvent $CDCl_3$. The mass spectra were registered on a Polaris Q/Trace GC Ultra (Ion Trap analyzer) (70 eV, ion source temperature 250°C, probe temperature 50–450°C).

The oxidation potentials of compounds **I**–**III** were measured by cyclic voltammetry on an IPC-pro potentiostat in a three-electrode cell in $CH_2Cl_2$ solutions ($c$ = 0.002 M) under argon. The working electrode was a stationary glassy carbon electrode ($d$ = 2 mm), the auxiliary electrode was a platinum plate ($S$ = 18 mm$^2$), and the reference electrode was Ag/AgCl/KCl with a waterPROOF diaphragm. The number of electrons transferred in an electrode process was estimated relative ferrocene. Potential sweep rate 0.2 V/s, supporting electrolyte 0.1 M $Bu_4NClO_4$.

All synthetic and analytical manipulations of the complexes were performed in evacuated ampules in oxygen-proof conditions.

Triphenylantimony (99%, Aldrich) and oleic acid (97%, Acros Organics) were used as received. Solvents were purified and dried by conventional procedures [18]. Compound **I** was synthesized as described in [5].

Complexes **II** and **III** were prepared by mixing 1 M solutions of 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzoquinone and corresponding triarylstibine in 30 mL of toluene. When the reaction mixture acquired a yellowing orange color, the solvent was evaporated in a vacuum. The residue was dissolved in hexane (15 mL). The solution was allowed to stand for 1 day at 0°C, and the fine crystals that formed were filtered off and dried in a vacuum. The yields in both cases were higher than 90%.

**Complex II.** $^1$H NMR spectrum (200 MHz), δ, ppm: 1.53 s (18 H, *t*-Bu), 3.70 s (6H, $OCH_3$), 7.47 d.m (6H, 4-$ClC_6H_4$, $J_{HH}$ 8.5 Hz), 7.65 d.m (6H, 4-$ClC_6H_4$, $J_{HH}$ 8.5 Hz). $^{13}$C NMR spectrum (50 MHz), $\delta_C$, ppm: 31.73 ($CH_3$, *t*-Bu), 36.22 (*t*-Bu), 60.75 ($OCH_3$), 125.46 [$\underline{C}_{Ar}(OCH_3)$], 129.63, 135.63, 136.00, 138.13 (4-$ClC_6H_4$), 141.05 [$\underline{C}_{Ar}$(*t*-Bu)], 145.55 (CO). Mass spectrum (EI), *m*/*z*: 734, 736, 738, 740.

**Complex III.** $^1$H NMR spectrum (200 MHz), δ, ppm: 1.54 s (18H, *t*-Bu), 3.70 s (6H, $OCH_3$), 7.19 t.m

(6H, 4-$FC_6H_4$, $J_{HF} = J_{HH}$ = 8.8 Hz), 7.72 d.d.m (6H, 4-$FC_6H_4$, $J_{HF}$ 5.7 Hz, $J_{HH}$ 8.8 Hz). $^{13}C$ NMR spectrum (50 MHz), $\delta_C$, ppm: 31.72 ($\underline{C}H_3$, *t*-Bu), 36.20 (*t*-Bu), 60.73 ($OCH_3$), 116.65 d (4-$FC_6H_4$, $J_{CF}$ 20.8 Hz), 125.35[$\underline{C}_{Ar}(OCH_3)$], 132.84 d (4-$FC_6H_4$, $J_{CF}$ 3.5 Hz), 136.89 d (4-$FC_6H_4$, $J_{CF}$ 8.1 Hz), 141.16 [$\underline{C}_{Ar}$(*t*-Bu)], 145.45 (CO), 164.76 d (4-$FC_6H_4$, $J_{CF}$ 252.6 Hz). Mass spectrum (EI), *m*/*z*: 686, 688.

Oxidation of oleic acid in the presence of compounds **I–III** was performed in a temperature-controlled cell at an air feed rate of 2–4 mL/min for 5 h. Since this reaction occurs as auto-oxidation, air was passed through the oleic acid solution for 2 h before adding compounds **I–III**. The concentration of the additives was 1 mM. The activity of the studied compounds during oxidation of oleic acid was estimated by a standard procedure by measuring the amount of isomeric hydroperoxides LOOH formed in the reaction [19].

## ACKNOWLEDGMENTS

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