

Synthesis and Properties of Triphenylantimony(V) Dithiolate Derivative

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Abstract—Interaction of substituted benzene-1,2-dithiols **I–III** with triphenylantimony(V) dichloride was studied. As a result of the exchange reaction of 3,6-dichlorobenzene-1,2-dithiol with Ph₃SbCl₂ in the presence of triethylamine triphenylantimony(V) 3,6-dichlorobenzene-1,2-dithiolate **IV** was obtained. Electrochemical properties of the free dithiols and the complex were explored. According to the cyclic voltammetry, the oxidation of the complex is irreversible and corresponds to one electron transfer with follow-up chemical stage. The antioxidant activity of compounds **I–IV** was examined in the process of oleic acid autoxidation. A more effective inhibition of the oleic acid oxidation was found at adding dithiol and better protective effect was observed in the presence of Ph₃SbCl₂ compared with the complex **IV**.

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We have previously shown that complexes of triphenylantimony(V) with catecholate and *o*-amidophenolate ligands exhibit an antiradical activity [1]. The common feature of these compounds is the ability to reversibly bind molecular oxygen [2–4]. The presence of electron-withdrawing substituents in the ligand favors the formation of the catecholates stable in air, while the antimony(V) complex containing donor groups can fix molecular oxygen [5]. The variation the nature of substances in the redox-active ligand affects the antioxidant capacity of these compounds in the process of free radical oxidation of unsaturated fatty acids and lipids. *o*-Amidophenolate and catecholate complexes of triphenylantimony(V) with donor groups prevent oxidation and promote the decomposition of hydroperoxides. In contrast to the above-mentioned compounds, the catecholate triphenylantimony(V) derivatives with acceptor substituents have only a short-term inhibitory effect.

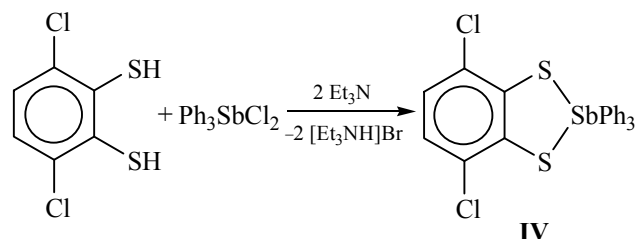
Study of electrochemical properties of the complexes showed that a correlation existed between the inhibition efficiency toward the oleic acid free radical oxidation and the compound oxidation potential: the easier it releases an electron, the higher its inhibition efficiency. Consequently, in the series of the triphenyl-

antimony(V) compounds containing a redox-active ligands the oxidation potential may be one of the defining characteristics of the antioxidant activity [6]. The structure of the previously studied complexes includes a five-membered metallocycle formed by the antimony(V) ion and a catecholate (*o*-amidophenolate) ligand capable of existing in several redox levels [7]. Replacing the heteroatoms in the ring for sulfur should affect significantly the properties of these compounds. Currently, the literature provides some examples of the antimony(III/V) dithiolate complexes [8, 9], but data on organometallic compounds of antimony(V) with sulfur-containing bidentate ligands have not been found.

In order to find new antimony compounds possessing unusual properties we carried out a reaction between triphenylantimony(V) chloride with benzene-1,2-dithiol (**I**), 4-methylbenzene-1,2-dithiol (**II**) and 3,6-dichlorobenzene-1,2-dithiol (**III**). We studied the electrochemical properties, antioxidant activity of free dithiols and the resulting complex **IV** in the inhibition of the oxidation of oleic (*cis*-9-octadeca-enoic) acid.

The exchange reaction of dithiols (**I–III**) with Ph₃SbCl₂ occurs in the presence of triethylamine. Under the anaerobic conditions the reaction with

dithiols **I** and **II** results in the formation of the solution of unstable dithiolate complexes which decomposes during the isolation. In contrast to the substituted *o*-amidophenolates and the triphenylantimony(V) catecholates that form spiroendoperoxides, the dithiolate antimony derivatives are oxidized by atmospheric oxygen to the triphenylantimony(V) oxide and the corresponding disulfides. The introduction of the acceptor atoms of chlorine in 3 and 6 positions of the aromatic ring of benzene-1,2-dithiol stabilizes dianionic S,S'-coordinated ligand, leading to the formation of complex **IV** which is stable to atmospheric oxygen.



Complex **IV** was isolated from toluene in a preparative yield. The compound was characterized by IR, ^1H , ^{13}C NMR, mass spectroscopy, its structure was fully consistent with the assumed formula.

The mechanism of the action of many antioxidants in the inhibition of free radical processes includes the hydrogen transfer or sequential deprotonation and loss of an electron, which leads to the formation of stable radicals of the antioxidant. The dissociation energy of the bond H–X (X is O, N, or S) determines the ease of the reaction with active radical. There are various experimental and computational methods for the determination of this indicator. One of experimental methods of assessment of the dissociation energies of H–X bond is a method that takes into account the values of the redox potential and the acid function [10]. The oxidation potential characterizes the reducing ability of the compound and is one of the factors determining the antioxidant activity. We investigated the electrochemical properties of complex **IV** and free dithiols **I–III** by the method of cyclic voltammetry (CV) (see the table).

In complex **IV** the central antimony atom is in the highest oxidation state, therefore, the observed electrochemical activity can be regarded as a change in the redox state of the coordinated ligand. In contrast to the previously studied triphenylantimony(V) catecholates [7], whose first anodic process is quasi-reversible, the dithiolate complex **IV** is characterized

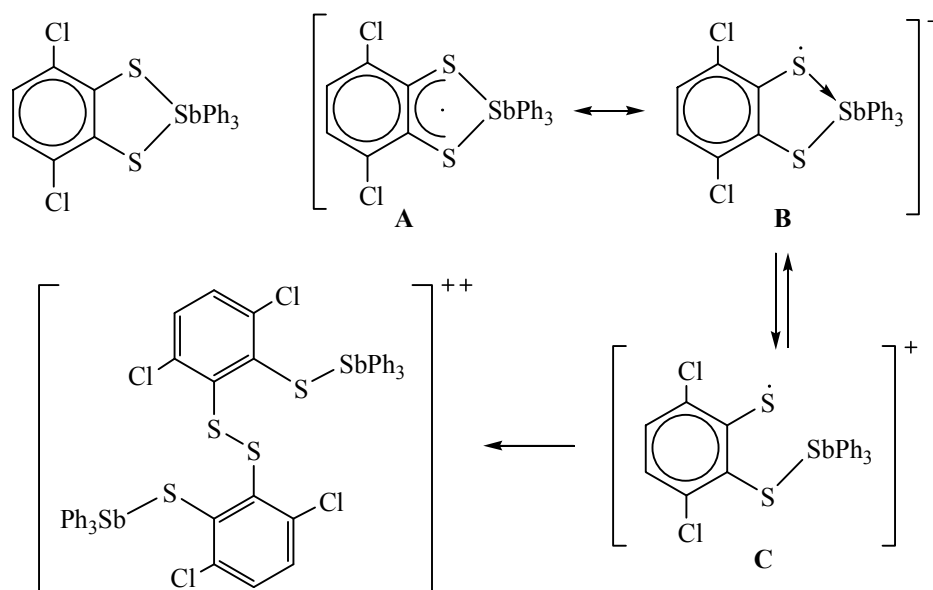
Oxidation potentials of dithiols **I–III** and complex **IV** measured by CV method on glassy carbon electrode, CH_2Cl_2 , $V = 0.2 \text{ V s}^{-1}$, $0.1 \text{ M NBu}_4\text{ClO}_4$, $c = 3 \times 10^{-3} \text{ mol L}^{-1}$, Ar, vs. $\text{Ag}/\text{AgCl}/\text{KCl}(\text{sat.})^a$

Compound	$E_{\text{pa}}^1, \text{V}$	n	$E_{\text{pa}}^*, \text{V}$
I	1.43	1.0	1.52
II	1.41	1.0	1.47
III	1.58	1.5	1.60
IV	1.46	1.0	–
$(\text{Cat}^{\text{Cl}})\text{SbPh}_3^b$	1.23	2.0	–

^a E_{pa}^1 is value of the peak potential of the first anodic process, E_{pa}^* is value of the peak potential of the first oxidation process obtained at the use of a platinum anode; n is the number of electrons transferred during the first anode stage versus ferrocene as a reference. ^b [5].

by two irreversible one-electron redox transition shifted to the anode area (Fig. 1). In the case of the oxygen-containing analog of compound **IV**, the triphenylantimony(V) 3,4,5,6-tetrahydrocatecholate $(\text{Cat}^{\text{Cl}})\text{SbPh}_3$, the introduction of the acceptor chlorine atoms in the catecholate ligand led to an increase in the number of electrons involved in the electrode reaction to two, and was accompanied by the decoordination of *o*-benzoquinone [7]. The oxidation of complex **IV** in the first step leads to the formation of an unstable intermediate radical cation, which can be represented as two resonance forms **A** and **B**.

The irreversible oxidation indicates a low degree of delocalization of the charge and spin in the aromatic ring and points to the predominant contribution of the localized form **B**, which is consistent with the known calculated data and the results of ESR studies of phenylthiyl radical [11]. Phenoxyl and phenylaminy radicals have delocalized structure [12], and in the case of the phenylthiyl radical, on the contrary, the localization of spin density on the sulfur atom is observed. Unsubstituted phenylthiyl radicals and monoanionic forms of the transition metal complexes with *o*-iminothiobenzosemiquinone radicals react to form dimeric disulfide adducts [11, 13]. The cation-radical intermediate **B** dissociates to form uncoordinated thiyl radical **C**, which dimerizes to form binuclear dication. The formation of a disulfide bond is reflected in the reverse scan of CV by a broad reduction peak at -0.2 V (Fig. 1a), presumably corresponding to the reduction of the disulfide complex. Similar changes in



CV were observed earlier for a series of transition metal complexes with coordinated thiophenolate anion [14]. The second anodic process registered in the voltammogram (Fig. 1b) at the potential $E_{pa} = 1.89$ V may equally correspond to further oxidation of the intermediate **B** accompanied by decoordination of the ligand, or to the oxidation of disulfide complex.

It is known that the oxidation of sulfur compounds

occurs at a more cathodic potential (0.05–0.1 V) than the corresponding oxygen analogs [14, 15]. On the contrary, the oxidation of compound **IV** occurs at a potential by 0.23 V higher than that of catecholate complex $(Cat^{Cl})SbPh_3$, which is not consistent with the results of electrochemical studies of the free ligands. As expected, the oxidation potential of benzene-1,2-dithiol is shifted to the cathode region (see the table) compared to pyrocatechol (1.48 V). This fact may indicate a more covalent character of the antimony–sulfur bond in the complex **IV** than the antimony–

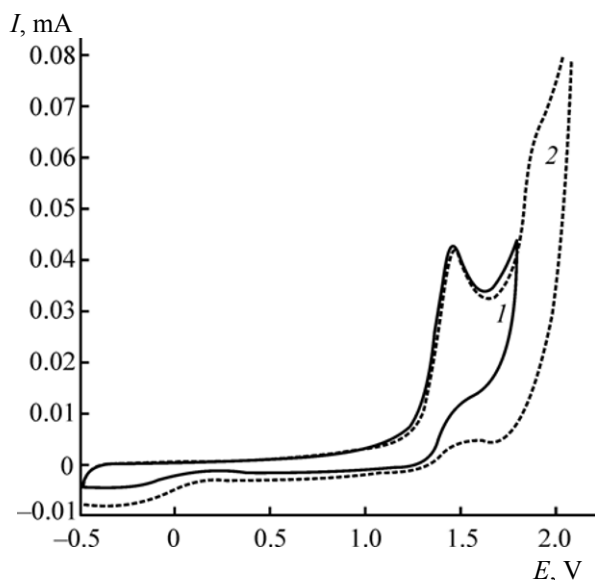
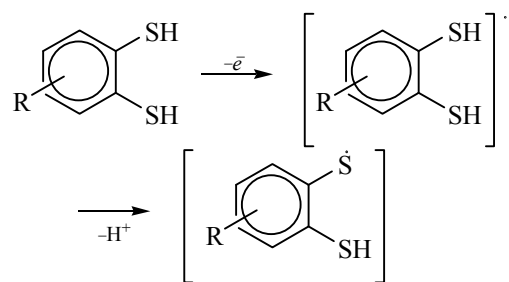


Fig. 1. CV of oxidation of complex **IV**; (1) in the range of potential sweep from -0.5 to 1.8 V, (2) in the range of potential sweep from -0.5 to 2.1 (CH_2Cl_2 , glassy carbon anode, $Ag/AgCl/KCl$, 0.1 M NBu_4ClO_4 , $c = 3 \times 10^{-3}$ M, argon).



oxygen bond in the catecholate derivative [14].

The electrochemical oxidation of dithiols on glassy carbon electrode is of irreversible one-electron type, and it leads to the formation of low stable radical cations.

After the electrode process the chemical stage of deprotonation takes place. The use of platinum anode allowed to observe on the voltammogram reverse branch the deprotonation step in all three dithiols

(−0.14 to −0.22 V). It should be noted that the values of oxidation potentials of dithiols **I–III** on the platinum anode are shifted to the anodic area, compared to the results for the carbon glass electrode (see table). The resulting thiyl radical is capable to enter into further dimerization reaction. The value of the oxidation potentials of dithiols **I–III** is affected by the nature of substituents on the phenyl ring: the electron-donor methyl group slightly shifts the oxidation potential to the cathode region, while the electron-withdrawing chlorine atoms impede the oxidation.

The reactivity and thermodynamic properties of free thiols determine a possibility of their application as electron carriers, antidotes for heavy metal poisoning, in the functioning of antioxidant protection systems of the body [16]. The interaction of thiols with free radicals through the hydrogen atom abstraction, as well as the reactivity of disulfides generated at the oxidation of thiols toward hydroperoxides allow the application of these compounds as inhibitors of free-radical processes. Based on the electrochemical data it is possible to predict that the greatest antioxidant activity should exhibit compounds **II**, **I** and **IV**.

The study of the oxidation of unsaturated fatty acids is a model reaction of lipid oxidation by peroxides in cell membranes. The oxidation of oleic acid (RH) with oxygen leads to the formation of substituted allyl radicals that interact with O_2 producing peroxy radicals $ROO^\bullet$. The corresponding *cis*- and *trans*-isomeric hydroperoxides ROOH are the main products in the initial stage of the oxidation process [17, 18]. In this paper we continue our study of antioxidant activity of the triphenylantimony(V) complexes with redox-active ligands and free ligands on a model example of oxidation of oleic [(*Z*)-octadec-9-enoic] acid at 60°C. In addition to studying the antioxidant activity of thiols **I–III**, we consider their chelating properties by an example of interaction with Ph_3SbCl_2 .

The results of investigation of the kinetics of accumulation of hydroperoxides are presented in Fig. 2. Adding a dithiol **I–III** or complex **IV** leads to a decrease in the concentration of hydroperoxide in the reaction medium. The explored dithiols show more pronounced inhibitory effect on the process of free radical oxidation of oleic acid during the time of the experiment as compared with complex **IV**. Based on the electrochemical data, the highest inhibitory activity would be expected in compound **II**, but dithiol **III** turned out to

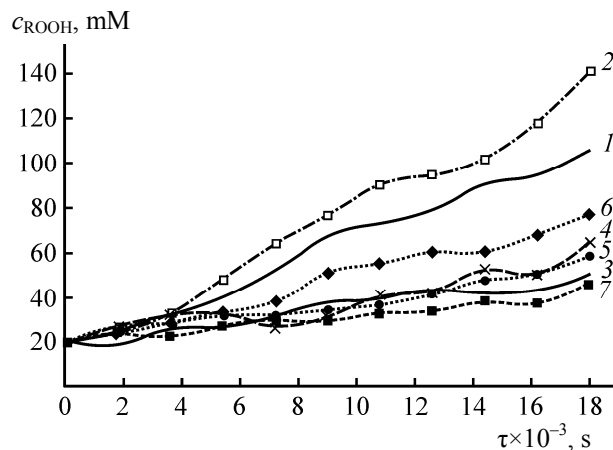


Fig. 2. Kinetic curves of accumulation of ROOH during the oxidation of oleic acid at 60°C in the presence of additives (1 mM): (1) no additives, Ph_3SbCl_2 (2), 3,6-dichloro-1,2-dithiobenzene (3), 1,2-dithiobenzene (4), 3-methyl-1,2-dithiobenzene (5), complex **IV** (6), 3,6-dichloro-1,2-dithiobenzene with Ph_3SbCl_2 (7).

be more effective inhibitor. The antimony(V) derivative Ph_3SbCl_2 (Fig. 2, curve 2) has a promoter effect increasing the content of hydroperoxides, which is consistent with previous results [19]. It is seen from Fig. 2, curve 7, that the promoting effect of Ph_3SbCl_2 may be obscured by the dithiol **III** additives which can act as a chelator. Obviously, the combined sulfur-containing ligand and Ph_3SbCl_2 has a more pronounced inhibitory effect on the concentration of hydroperoxides than synthesized complex **IV**. Comparative data on the antioxidant activity of the compounds in the autoxidation of oleic acid at 60°C within 5 h are shown in Fig. 3.

The analysis of the results showed that the maximum activity among the studied dithiols have the substituted dithiobenzenes **II** and **III**. The inhibitory activity of dithiols is due to the homolytic decomposition of S–H bond at the action of active $ROO^\bullet$ radicals. The dimerization of thiyl radicals leads to the formation of disulfides, which are capable of further oxidation at the SH group and can destruct hydroperoxides forming sulfoxides [16]. Complex **IV** is a one-electron donor forming at the oxidation a dicationic compound inactive toward hydroperoxy radicals, unlike disulfides formed at the oxidation of the ligands.

Thus, in this work we obtained a new dithiolate complex of triphenylantimony(V) **IV** stable stable

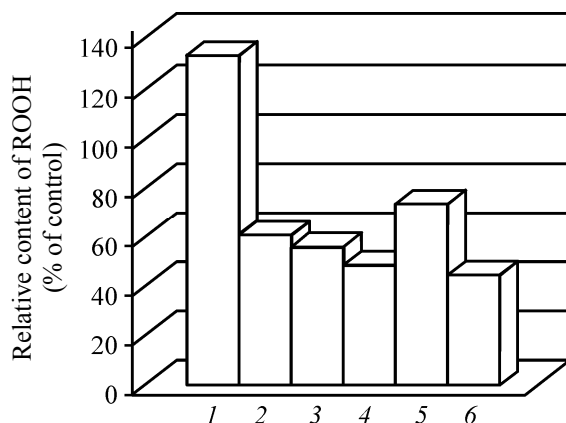


Fig. 3. Relative content of ROOH in oleic acid in the course of 5 h autoxidation at 60°C; additive concentration (1 mM): (1) Ph₃SbCl₂; (2) benzene-1,2-dithiol, (3) 4-methyl-1,2-dithiobenzene, (4) 3,6-dichloro-1,2-dithiobenzene, (5) complex IV, (6) 3,6-dichloro-1,2-dithiobenzene + Ph₃SbCl₂. ROOH content in oleic acid without additives is taken as 100%.

under aerobic conditions, studied the redox properties of dithiols **I–III** and complex **IV**, and estimated their activity by the example of autoxidation of oleic acid. According to the cyclic voltammetry the oxidation of dithiols **I–III** and complex **IV** is irreversible and proceeds as a one-electron transfer with follow-up chemical stage. Unlike triphenylantimony(V) catecholates, the oxidation of complex **IV** results in an unstable monocationic form of the complex capable of further dimerization. Replacing heteroatoms in the metallocycle, in particular, oxygen by sulfur in the complex **IV** results in the formation of structures with the spin density localized on the sulfur atom. Lack of delocalization of the electron density over the aromatic moiety reduces the effectiveness of the antioxidant action of complex **IV**. We found that adding compounds **I–IV** leads to the inhibition of the oleic acid oxidation indicating that they possess an antioxidant activity. The relative content of oleic acid hydroperoxides in the presence of dithiols **I–III** is significantly lower compared to complex **IV**, and the free dithiol **III** shows the maximum effect.

EXPERIMENTAL

Commercially available reagents: benzene-1,2-dithiol (Aldrich, 96%), 4-methyl-1,2-dithiobenzene (Fluka, 97%), 3,6-dichloro-1,2-dithiobenzene (Sigma–Aldrich, 95%) Ph₃SbCl₂ (Aldrich, 99%), 1,2-dihydroxybenzene (chemically pure), oleic (*cis*-9-octadecanoic) acid from Acros Organics, 97% were used

without further purification. The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE DPX-200 spectrometer, internal reference TMS, solvent CDCl₃. IR spectra were recorded on a FT-IR spectrometer FSM 1201 from samples in mineral oil. The mass spectra of compounds were recorded on a mass spectrometer Polaris Q/Trace GC Ultra (Ion Trap analyzer), 70 eV, ion source temperature 250°C, the sample temperature 50–450°C. Experiments on the synthesis and studying the properties of the complex were carried out in evacuated ampules in the absence of oxygen. Used solvents were purified and dried freed by usual technique [20].

Complex IV. To a solution of triphenylantimony dichloride (0.256 g, 0.5 mmol) in 40 mL of toluene was added with stirring a solution of 3,6-dichlorobenzene-1,2-dithiol (0.106 g, 0.5 mmol) in 30 mL of toluene and then a solution of triethylamine (0.14 mL, 1.0 mmol) in 10 mL of toluene. The reaction mixture was stirred at room temperature for 3 h, the solution was concentrated to about 1/4 of the volume, 20 mL of hexane was added, and the solution was left overnight at –18°C. The solution was filtered from the formed triethylammonium chloride precipitate, and the solvent was replaced by hexane (~30 mL). At standing this solution for two days at –18°C a powdery precipitate of the complex formed, which was filtered off, washed twice with hexane, and dried in a vacuum. Yield 0.23 g (81.8%). IR spectrum (vaseline oil, cm^{–1}): 1572 m, 1528 m, 1476 m, 1432 s, 1396 s, 1365 w, 1326, 1303 w, 1262 w, 1239 m, 1187 w, 1179 w, 1158 s, 1116 w, 1075 s, 1067 s, 1061 s, 1019 w, 997 s, 913 w, 820 m, 805 m, 799 m, 773 w, 731 s, 727 s, 695 s, 688 s, 600 m, 553 m, 510 w, 500 w, 490 w, 464 m. ¹H NMR spectrum (200 MHz, δ, ppm): 7.02 s (2H, C₆H₂), 7.39–7.49 m (9H, Ph), 7.65–7.69 m (6H, Ph). ¹³C NMR spectrum (50 MHz, δ, ppm): 124.66 (CH_{Ar}), 129.40 (Ph), 130.54 (CCl_{Ar}), 130.88 (Ph), 133.80 (Ph), 137.50 (CS_{Ar}), 139.83 (Ph). Mass spectrum (EI): 560, 562, 564, 566 ([M]⁺: ¹²¹Sb, ¹²³Sb, ³⁵Cl, ³⁷Cl).

Measurement of oxidation potentials of compounds **I–IV** was performed by cyclic voltammetry (CV) in a three-electrode cell using the potentiostat IPC-pro, in acetonitrile, under argon. The working electrode was a stationary glassy carbon (GC) (platinum) with a diameter of 2 mm, auxiliary electrode was a platinum plate (*S* = 18 mm²). The reference electrode was (Ag/AgCl/KCl) with a waterproof diaphragm. The concentration of the substance is 0.003 M. The number of electrons transferred in the

electrode process was evaluated relative versus ferrocene as a reference. Potential sweep rate 0.2 V s^{-1} . The supporting electrolyte $0.1 \text{ M Bu}_4\text{NClO}_4$ (Acros Organics, 99%).

Oxidation of oleic acid in the presence of compounds **I–IV** was carried out in a temperature-controlled cell (60°C) at a rate of air flow $2\text{--}4 \text{ mL min}^{-1}$ for 5 h. Since the oxidation of oleic acid occurs as an autoxidation, a 2 h preliminary bubbling of air was performed before adding a compound. Concentration of additives was 1 mM . Activity of the compounds in the oxidation of oleic acid was estimated by the standard method by the amount of isomeric ROOH hydroperoxides formed [21].

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