ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 5, pp. 273–279. © Pleiades Publishing, Ltd., 2014.
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Trialkylantimony(V) *o*-Amidophenolates: Electrochemical Transformations and Antiradical Activity

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Received August 12, 2013

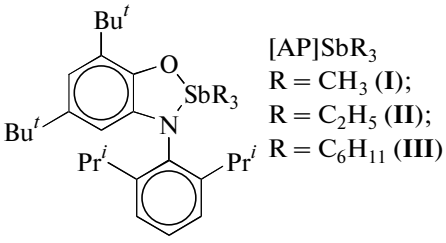
Abstract—The electrochemical transformations and antiradical activity of trialkylantimony(V) *o*-amidophenolate derivatives, (AP)SbR_3 (AP = 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-amidophenolate); R = CH_3 (**I**), C_2H_5 (**II**), and C_6H_{11} (**III**), are studied. The electrochemical oxidation of compounds **I**–**III** proceeds successively to form mono- and dicationic forms of the complexes. The presence of the donor hydrocarbon groups at the antimony(V) atom shifts the oxidation potentials to the cathodic range and decreases the stability of the monocationic complexes formed in electrochemical oxidation. The second anodic process is irreversible and accompanied by *o*-iminoquinone decoordination. The antiradical activity of compounds **I**–**III** is studied in the reaction with the diphenylpicrylhydrazyl radical and oleic acid autooxidation. The values obtained for indices EC_{50} and IC_{50} indicate the antiradical activity of the studied compounds. Complexes **I**–**III** were found to be the efficient inhibitors of oleic acid oxidation and act as efficient destructors of hydroperoxides.

DOI: 10.1134/S107032841405011X

INTRODUCTION

A new approach based on the modification of structures of compounds by the introduction of metal atoms is being developed in the antioxidant chemistry [1]. Syntheses of low-molecular-weight metal-containing antioxidants and studies of their biological activity *in vitro* and *in vivo* is caused by their anti-inflammatory and neuroprotective action and antiradical activity; and these objects can be considered as promising chemopreventive agents [2–4]. A search for biologically active substances in a series of organometallic derivatives of nontransition metals is related to their ability to manifest both anti- and prooxidant properties, depending on the method of introduction and the place and time of their application. The organometallic antimony(V) derivatives attract attention due to a variety of coordination modes and promising biological properties [5–7].

Toxicity and physiological response of organometallic compounds depend on the oxidation states of both the metal and organic ligands to which the metal is bound. The variation of the ligand environment affects significantly the properties of the formed compounds [8]. The variation of the ligand nature and the redox state of the metal center is a possibility to control the thermodynamic and kinetic characteristics and the biological activity of the complexes. One of the currently developed trends in bioinorganic chemistry is the complex formation of pharmacologically active organic substrates with organometallic derivatives of transition metals [9, 10]. The result of such a symbiosis is the manifestation of a new type of activity or the modulation of the known one [11]. Organic ligands can be centers of redox reactions in addition to the metal center. Examples of this type of ligands are sterically hindered phenol derivatives, catecholates, aminophenols, polyphenols, and flavonoids. The redox properties and antiradical activity of the trialkylantimony(V) *o*-amidophenolate derivatives (Scheme 1) were studied in the present work.



[AP]SbR_3
R = CH_3 (**I**);
R = C_2H_5 (**II**);
R = C_6H_{11} (**III**)

Scheme 1.

Several centers can be distinguished in the structure of the studied molecules: the redox-active organic fragment, antimony(V) atom, and hydrophobic organic groups. Sterically hindered *o*- and *p*-aminophenols are redox-active molecules and can manifest either pro- or antioxidant activity, depending on

conditions [12]. Hydroxyanthranilic acid is a natural prototype of *o*-aminophenols and one of physiologically active compounds capable of acting as the second line of antioxidant protection after ascorbate and ubiquinone that provide the protection of low-density lipoproteins from both radical and nonradical oxidants [13]. The introduction of the sterically hindered *o*-aminophenolate fragment into the structures of the studied objects can considerably increase the reductive activity of the compounds.

The study of the electrochemical behavior of organometallic compounds makes it possible to model reactions with oxidants and to monitor products formed due to the interaction. As shown earlier for a series of the triphenylantimony(V) complexes with the redox-active ligands, the variation of substituents in the carbon aromatic ring or the replacement of the heteroatom in the metallocycle allow to control the potential of the catecholate(*o*-amidophenolate)/*o*-semiquinone(*o*-iminosemiquinone) transition, thus facilitating or impeding oxidation [14, 15]. In this work, we are intending to evaluate the influence of the hydrocarbon groups at the antimony atom on the redox transformations of the (AP)SbR_3 complexes (AP = 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-amidophenolate; R = CH_3 (**I**), C_2H_5 (**II**), and C_6H_{11} (**III**)) and their antiradical activity in the reactions with the diphenylpicrylhydrazyl radical and in the inhibition of oleic (*cis*-9-octadecenoic) acid oxidation.

The existence of several redox forms of the ligand (*o*-amidophenolate/*o*-iminosemiquinolate/*o*-iminobenzoquinone) and the presence of donor hydrocarbon groups at the antimony(V) atom and labile Sb–C bonds provides a dual anti/prooxidant behavior of similar compounds.

EXPERIMENTAL

Synthesis of trimethylantimony(V) (*N*-(2,6-diisopropylphenyl)-4,6-di-*tert*-butyl-*o*-amidophenolate) (AP)$SbMe_3$ (I). A portion of a 1 M solution of Me_3Sb in toluene was added dropwise with stirring to a solution of *N*-(2,6-diisopropylphenyl)-4,6-di-*tert*-butyl-*o*-iminobenzoquinone (0.250 g, 0.66 mmol) in toluene (15–20 mL) until the cherry color of the solution turned yellow completely. Toluene was evaporated in vacuo, and the residue was heated at 50°C for 20 min and then dissolved in pentane (20 mL). The obtained solution was cooled to –12°C and stored at this temperature for 24 h, a finely crystalline pale yellow powder of complex **I** was obtained. The yield was 0.295 g (82%).

IR (ν, cm^{-1}): 1567 m, 1442 s, 1419 s, 1365 m, 1334 m, 1320 m, 1288 s, 1245 s, 1222 w, 1200 m, 1176 w, 1122 w, 1101 w, 1051 m, 1040 w, 1025 m, 995 s, 926 m, 904 m, 861 m, 851 s, 823 s, 803 s, 771 m, 762 m, 712 m, 679 w, 652 m, 606 w, 585 w, 555 m, 544 w, 528 s, 511 s, 481 m, 450 w, 431 w. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C), δ, ppm: 1.06 (s, 9H, *t*-Bu), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 2 $CH(CH_3)_2$), 1.12 (s, 9H, *t*-Bu), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 2 $CH(CH_3)_2$), 1.44 (s, 9H, $SbMe_3$), 3.15 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, 2 $CH(CH_3)_2$), 5.83 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 6.58 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2); 7.14–7.37 (m, 3H, C_6H_3).

For $C_{29}H_{46}NOSb$

anal. calcd., %:	C, 63.74;	H, 8.48;	N, 2.56;	Sb, 22.28.
Found, %:	C, 64.01;	H, 8.53;	N, 2.29;	Sb, 22.15.

Compounds **II** and **III** were synthesized using described procedures [16, 17].

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX-200 spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. IR spectra were measured on an FSM 1201 FT-IR spectrometer in Nujol. Experiments on syntheses of the complexes were carried out in evacuated ampules without oxygen. Absorption spectra were recorded on an SF-103 spectrophotometer in a range of 220–1100 nm at room temperature. EPR spectra were detected on a Bruker EMX spectrometer at a working frequency of ~9.5 GHz. Hyperfine coupling constants were determined using the simulation of theoretical spectra by the Simfonia program (Bruker). The solvents used were purified and degassed using standard procedures [18].

Commercial reagents (2,2-diphenyl-1-picrylhydrazyl (DPPH) radical (Aldrich), $[(C_5H_5)_2Fe]BF_4$ (Aldrich), and oleic (*cis*-9-octadecenoic) acid (97%, Acros Organics)) were used without additional purification.

The electrochemical potentials of the studied compounds were measured by cyclic voltammetry (CV) in a three-electrode cell using an IPC-pro potentiostat in dichloromethane under argon. The stationary glassy-carbon (GC) electrode with a diameter of 2 mm was used as a working electrode, and a platinum wire (S = 18 mm^2) served as an auxiliary electrode. The reference electrode (Ag/AgCl/KCl) was equipped with a water-impervious membrane. The concentration of compounds **I–III** was 0.003 mol/L. The number of electrons transferred in the electrode process was estimated versus ferrocene as a standard. The potential scan rate was 0.2 V/s. The supporting electrolyte was 0.1 M Bu_4NClO_4 (99%, Acros). The microelectrolysis of complex **II** was carried out using a PI-50-1.1 potentiostat on stationary platinum electrodes (plates with a surface area of 30 mm^2) in an undivided three-electrode cell (2 mL) at a potential of 0.6 V (electrolysis time 3 h, conversion of the complex 84%). The Ag/AgCl/KCl electrode with an electroconducting water-impervious membrane was used as a reference electrode. Complex **II** (c = 0.003 mol/L) was added to a predeaerated electrochemical cell containing a solution

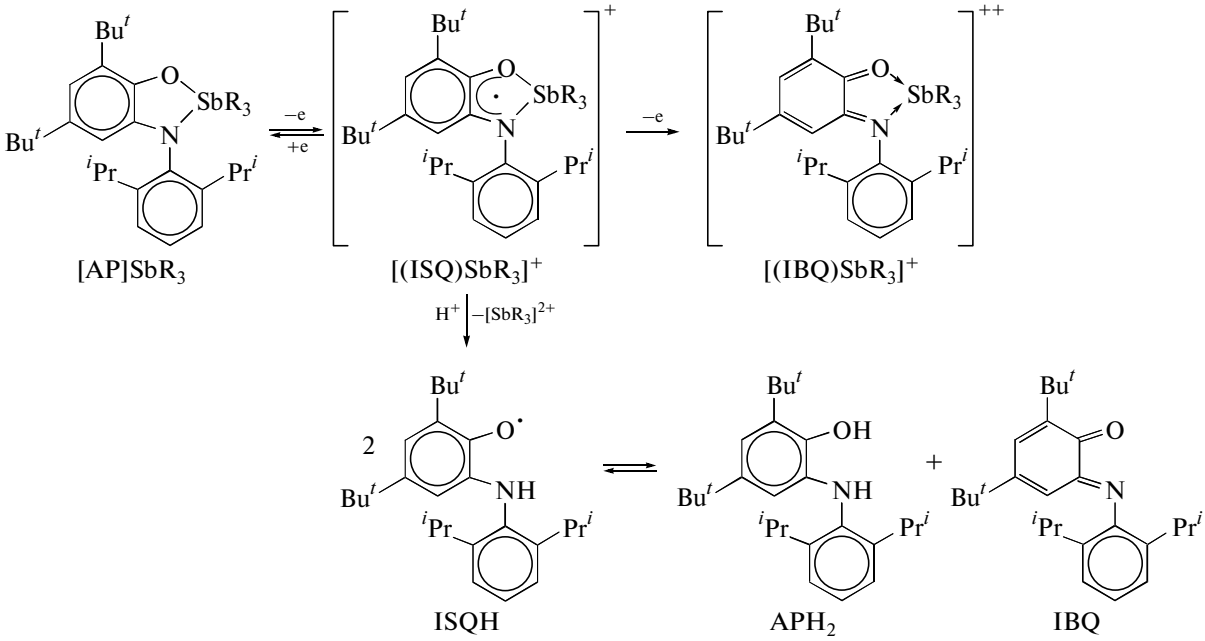
of the supporting electrolyte (0.1 mol/L n-Bu_4NClO_4) in dichloromethane.

The antiradical activity of complexes **I–III** in the reactions with the DPPH radical in dichloromethane was determined using a described procedure [4]. Oleic acid was oxidized in the presence of compounds **I–III** in a temperature-controlled cell (60°C) at an air flow rate of 2–4 mL/min for 5 h. Since oleic acid oxidation proceeds as autooxidation, preliminary air bubbling was carried out for 2 h before the compounds were introduced. The concentration of the additives was 1 mmol/L. The activity of the studied compounds during oleic acid oxidation was estimated by a standard method from the amount of formed isomeric hydroperoxides (LOOH) [19].

The index of inhibition efficiency (IE) for oleic acid autooxidation was determined by the formula $IE = [(1 - c_i/c_0) \times 100\%]$, where c_i is the concentration of hydroperoxides in the presence of an additive of the complexes (1 mmol/L), and c_0 is the content of LOOH formed in the control sample for 5 h. The IC_{50} index is the inhibitor concentration necessary for decreasing the concentration of hydroperoxides by 50% of the initial level for 5 h of oleic acid autooxidation. To determine IC_{50}, the concentration of complexes **I–III** was varied from 0.01 to 1 mmol/L. Therefore, the lower the IC_{50} index, the higher the antiradical activity of the complexes. The results are presented as average values of three independent experiments.

RESULTS AND DISCUSSION

The electrochemical properties of the antimony(V) compounds were studied by the CV method (Table 1). Complexes **I–III** are oxidized at the GC electrode in dichloromethane in two successive stages. The first redox transition for the studied complexes is the quasi-reversible one-electron process. The cyclic voltammogram for the oxidation of the triethylantimony 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-amidophenolate complex (**II**) is shown in Fig. 1. For compounds **I–III**, the first anodic process corresponds to the change in the redox state of the coordinated ligand: the *o*-amidophenolate (AP)–*o*-iminobenzosemiquinone (ISQ) transition occurs to generate monocationic complexes $[(ISQ)SbR_3]^+$ in the near-electrode region (Scheme 2).



Scheme 2.

Unlike the earlier studied triphenylantimony complex (AP)$SbPh_3$ (**IV**), compounds **I–III** are characterized by a decrease in the reversibility coefficient (I_c/I_a) (Table 1), indicating a decrease in the stability of the monocationic forms of the complexes formed in the electrochemical reaction. The chemical stage following the electron transfer occurs in the near-electrode region (Scheme 2). This conclusion is confirmed by the irreversible cathodic peak in the reverse branch of the voltammogram (–0.82 V) corresponding to the product of the destruction of complexes, which is formed after the first anodic stage.

Unlike complexes **I–III**, this peak for compound **IV** appeared only after the second redox process that characterizes the formation of the dicationic complex. The detected cathodic process corresponds to the reduction of decoordinated *o*-iminobenzoquinone (**IBQ**) (Fig. 1) formed due to the disproportionation of

Table 1. Oxidation potentials of the antimony(V) complexes according to the CV method*

Compound	$E^1_{1/2}$, V	I_c/I_a	n	E^2_p, V	n
(AP)$SbMe_3$ (**I**)	0.41	0.63	1.0	0.97	$n < 1$
(AP)$SbEt_3$ (**II**)	0.41	0.71	1.0	0.98	$n < 1$
(AP)$Sb(C_6H_{11})_3$ (**III**)	0.35	0.78	1.0	1.17	$n < 1$
(AP)$SbPh_3$ (**IV**) [15]	0.50	0.94	1.0	1.27	1.0

* GC electrode, CH_2Cl_2, $V = 0.2$ V/s, 0.1 M NBu_4ClO_4, $c = 3 \times 10^{-3}$ mol/L, Ar, vs. Ag/AgCl/KCl (sat.); $E^1_{1/2}$ is the half-wave potential of the first anodic process, I_c/I_a is the ratio of currents of the reverse cathodic and direct anodic peaks, n is the number of electrons transferred during the redox process relatively to ferrocene as a standard, and E^2_p is the potential of the oxidation peak of the second anodic process.

the *o*-aminophenoxyl radical (**ISQH**). The microelectrolysis of complex **II** at the controlled potential (0.6 V) is accompanied by the colorization of the solution. A new band corresponding to the formation of sterically hindered *o*-iminobenzoquinone appears in the visible range (λ_{max} = 390 nm) in the absorption spectrum [20].

The reaction of compound **I** with ferrocenium tetrafluoroborate ([Fc][BF_4]) as a one-electron oxidant was carried out at reduced temperature to confirm the oxidation mechanism of the complexes. The oxidation of compound **I** is accompanied by the appearance of the EPR spectrum (g_i = 2.0023) with a weakly resolved structure (Fig. 2). The spectrum detected at a lowered temperature (203–243 K) is a superposition of signals from two paramagnetic species: the cationic complex [(ISQ)$SbMe_3$][BF_4] and *o*-aminophenoxyl radical (ISQH) [21]. Compound **I** is oxidized with the decomposition of the monocationic complex accompanied by the decoordination and protonation of the *o*-iminobenzosemiquinone radical anion. The temperature increase results in the disappearance of the signal from [(ISQ)$SbMe_3$][BF_4] and an increase in the intensity of the signal from ISQH radical.

The electrochemical oxidation of compounds **I** and **II** at the first stage is accompanied by *o*-iminobenzoquinone decoordination and also by the evolution of gaseous products at the auxiliary electrode. Similar phenomena were earlier detected for the triethylantimony(V) complexes with the redox-active ligands [22, 23]. Evidently, the electron transfer results in the cleavage of the labile Sb–C bond [24] leading to the liberation of active methyl and ethyl radicals that undergo further reactions: recombination on the surface of the auxiliary electrode or interaction with the solvent.

The extension of the potential scan range to the anodic region results in the detection of the second oxidation stage (Fig. 1). This redox transition for complexes **I–III** is irreversible and corresponds to the transformation of the *o*-iminobenzosemiquinone

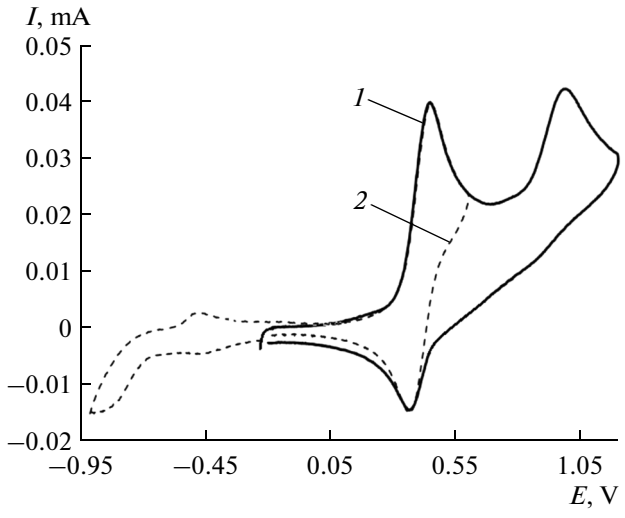


Fig. 1. Cyclic voltammogram of the oxidation of complex **II** at the potential scan (*1*) from –0.20 to 1.20 V and (*2*) from –0.92 to 0.60 V (CH_2Cl_2, GC anode, Ag/AgCl/KCl, 0.1 M NBu_4ClO_4, $c = 3 \times 10^{-3}$ mol/L, argon).

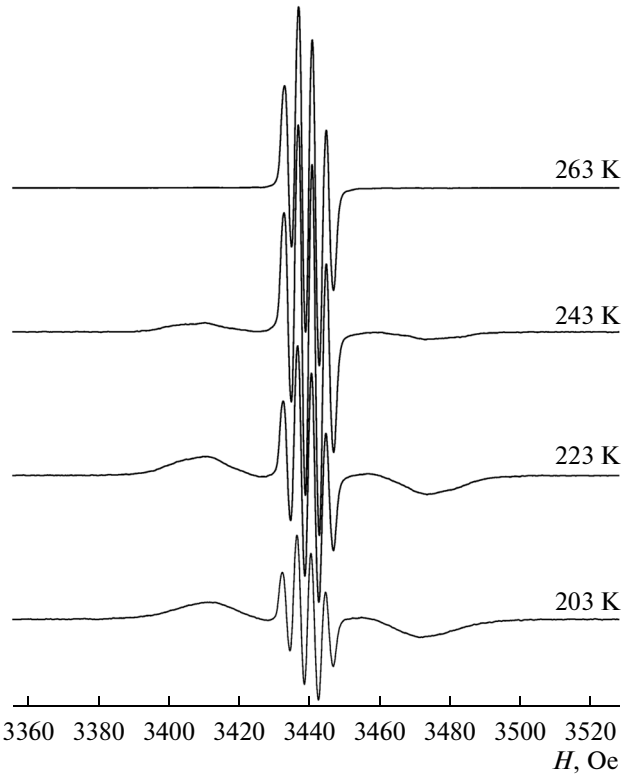


Fig. 2. EPR spectrum of the (AP)$SbMe_3$–[Fc][BF_4] system (THF, temperature increase from 203 to 263 K).

form of the ligand (ISQ) into the *o*-iminobenzoquinone form (IBQ) to produce the corresponding dicationic complexes $[(IBQ)SbR_3]^{++}$ unstable in the time scale of CV experiment. The number of transferred electrons is less than one, which is caused by chemical transformations of intermediates formed in the first redox stage. The obtained results indicate the overall decrease in the stability of the oxidized forms of complexes **I–III** compared to the triphenylantimony(V) derivatives containing the *o*-amidophenolate ligand.

The value of the oxidation potential of the complexes is affected by the nature of groups at the antimony atom: electron-donor alkyl substituents shift the $E^1_{1/2}$ parameter to the cathodic region, and the maximum effect is observed for the cyclohexyl group (the potential shift compared to that of complex **IV** is 0.15 V). The oxidation potentials remain unchanged on going from methyl-substituted complex **I** to complex **II**.

The CV method makes it possible to study redox transformations of organometallic compounds and also to predict their antiradical activity *in vitro*. The easier the oxidation, the higher the reducing properties and the probability of interaction with active species. Therefore, most easily oxidizable complexes **I–III** should be more efficient radical scavengers than a similar triphenylantimony(V) *o*-amidophenolate complex. However, the possibility of the homolytic cleavage of the Sb–C bond in the course of oxidation of the studied compounds and, hence, the generation of active alkyl radicals can result in the prooxidant effect.

It has earlier been shown that the triphenylantimony(V) complexes with the catecholate and *o*-amidophenolate ligands manifest the antiradical activity [4]. Experiments with the DPPH radical were carried out to establish the influence of substituents at the antimony atom on the antiradical activity of the studied compounds and its ability to exhibit the dual anti/prooxidant properties and the activity of complexes **I–III** in the inhibition of oleic acid oxidation was estimated.

The reactions of the DPPH radical with compounds **I–III** were carried out in a deaerated solution of CH_2Cl_2 at 298 K. The introduction of complexes **I–III** into a solution containing the DPPH radical decreases the intensity of the absorption maximum at 527 nm, indicating that the reaction occurs (Table 1). The possibility of occurrence of the reaction between the complexes and DPPH radical assumes their ability to act as efficient radical interceptors, which is confirmed by the obtained values of EC_{50} (Table 2). The minimum value of EC_{50} was obtained for complex **II**. The indices of antiradical activity of complexes **I–III** are close to the data for *p*-alkylaminophenols [25].

The study of the antiradical activity of the studied compounds was continued for the autooxidation of oleic (*cis*-9-octadecenoic) acid at 60°C. The peroxide oxidation of a substrate was controlled by the change in the concentration of hydroperoxides (LOOH), the major products of the primary stage of oxidation. The introduction of additives of compounds **I–III** decreases the initial level of hydroperoxides (Fig. 3, curves *1–3*). Then the LOOH concentration remains almost unchanged during the experiment and increases regularly in the control experiment (Fig. 3, curve *4*).

Table 2. Antiradical activity of compounds **I–IV** in a test with the DPPH radical (CH_2Cl_2, 298 K) and in the autooxidation of oleic acid*

Compound	EC_{50}, μmol	IC_{50}, μmol	EI, %
$(AP)SbMe_3$ (**I**)	18.9 ± 1.2	21.0 ± 0.9	92.7
$(AP)SbEt_3$ (**II**)	13.7 ± 0.8	19.5 ± 1.2	94.4
$(AP)Sb(C_6H_{11})_3$ (**III**)	17.6 ± 0.6	21.2 ± 0.7	97.8
$(AP)SbPh_3$ (**IV**) [4]	9.0 ± 1.3		97.5

* EC_{50} is the index of antiradical activity of complexes **I–IV** in the reaction with the DPPH radical, IC_{50} is the minimum concentration of the antimony(V) complexes resulting in a decrease in the hydroperoxide content by 50% of the initial level, and IE is the index of inhibition efficiency for the autooxidation of oleic acid.

The addition of complexes **I–III** exerts an inhibition effect on the development of the radical chain process compared to the control experiment. In the presence of the studied complexes, the amount of LOOH does not increase but, vice versa, they decompose. The comparative data on the efficiency of the inhibition effect of complexes **I–III** are presented in Table 2. All complexes exhibit high inhibition activ-

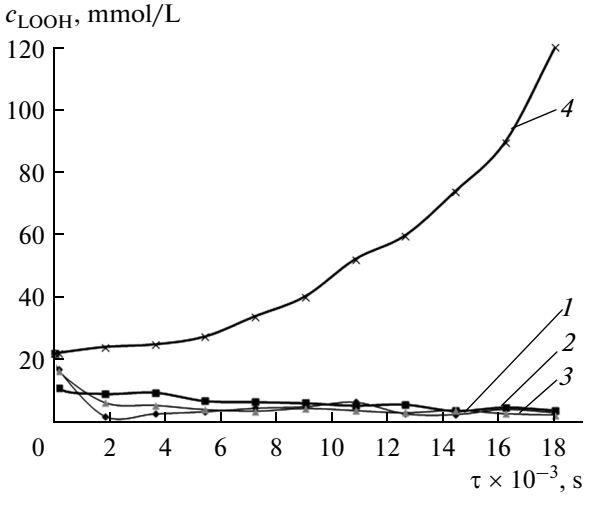


Fig. 3. Kinetic curves of LOOH accumulation in the oxidation of oleic acid at 60°C in the presence of additives (1 mmol/L) of (*1*) $(AP)SbMe_3$, (*2*) $(AP)SbEt_3$, and (*3*) $(AP)Sb(C_6H_{11})_3$ and (*4*) without additives.

ity. Nearly identical values were detected for compounds **III** and **IV** containing cyclohexyl and phenyl groups.

The activity of complexes **I–III** during LOOH decomposition is clearly demonstrated by the IC_{50} index determined in the experiment with oleic acid preliminarily subjected to autooxidation (60°C, 5 h) with a high initial concentration of hydroperoxides. The variation of concentrations of compounds **I–III** made it possible to establish the minimum values at which the LOOH concentration decreased by 50%. For complexes **I–III**, the IC_{50} indices are observed in the micromolar concentration range and are close. All complexes demonstrate high activity in the inhibition of oleic acid oxidation. The studied trialkylantimony(V) *o*-amidophenolates can be considered as inhibitors of the radical chain process and also as efficient destructors of hydroperoxides.

The organometallic derivatives of antimony (Ph_3Sb, Ph_3SbHal_2) and tin (R_2SnHal_2, R_3SnHal, R_nSnL_{4-n}) are known as promoters of the peroxidation of unsaturated fatty acids and lipids [4, 26–29]. The such behavior is caused by the easy cleavage of the σ-M–R bond upon the interaction with the LOO radicals. The indirectly detected products of the partial decomposition of complexes **I** and **II** ($CH_3^{\bullet}$, $C_2H_5^{\bullet}$) formed due to electrochemical oxidation are potential initiators of the radical chain oxidation of unsaturated substrates. However, the experiments involving compounds **I–III** indicate the absence of a promoting effect. Similar results have recently been obtained for the organotin compounds containing the fragment of sterically hindered phenol [30].

The studied complexes act as efficient inhibitors of oxidation and favor the decomposition of hydroperoxides. This activity is mainly caused by the donor ligand able to exist in several redox states. However, the efficiency of inhibition of oleic acid oxidation in the presence of the free ligand 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-aminophenol (APH_2) is 71.2%, which is significantly lower than that for the studied complexes [4]. Therefore, the organometallic fragment, namely, the nature of hydrocarbon groups at the antimony atom, also affects the reactivity of compounds **I–IV**. In spite of more cathodic oxidation potentials, compounds **I–III** are characterized by lower values of EC_{50} and IC_{50} compared to those of triphenylantimony *o*-amidophenolate $(AP)SbPh_3$. In addition, the above electrochemical data show that the replacement of the phenyl groups by alkyl groups decreases the stability of the monocationic complexes. The insignificant decrease in the antiradical activity of compounds **I–III** compared to that of compound **IV** is due to a lower stability of the monocationic complexes as the major intermediates formed upon oxidation.

The redox properties and reactivity of the antimony(V) complexes change with the variation of the redox-active ligands and also depend on the nature of the hydrocarbon groups at the antimony atom. For complexes **I–III**, the introduction of donor groups shifts the oxidation potentials to the cathodic region, and the stability of the oxidized forms of the complexes decreases considerably. The lability of the Sb–C bond assumes that active intermediates capable of intensifying the development of radical chain oxidation are generated in the oxidation process. However, the obtained values of EC_{50} and IC_{50} indicate the manifestation of the antiradical activity of complexes **I–III**. Evidently, the presence of the redox-active *o*-amidophenolate ligand plays the key role in the inhibition effect of these compounds, and the nature of the hydrocarbon groups at the antimony atom exerts a minor effect on the total antiradical activity.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (projects nos. 12-03-31026 and 13-03-00487) and the President of the Russian Federation (grants nos. MK-445.2014.3, NSh-271.2014.3).

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Translated by E. Yablonskaya