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Electromediators Based on the Ni(II) and Cr(III) Complexes with the Redox-Active Ligands in the Synthesis of Sulfur-Containing Organic Compounds

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Abstract—The chromium(III) tris-*o*-semiquinolate complex $Cr(L^{SQ})_3$ (L^{SQ} is 3,6-di-*tert*-butyl-*o*-semiquinone) and the monoanionic paramagnetic nickel(II) complex $[n\text{-}Bu_4N][Ni(L_S^{SQ})(L_S^{DT})]$ (L_S^{SQ} is *o*-thiosemiquinone, L_S^{DT} is benzene-1,2-dithiolate) are considered as electromediators of hydrogen sulfide oxidation in the presence of various organic substrates (hex-1-ene, oct-1-ene, benzene, toluene, and benzoic acid). It is revealed that the electrolysis of hydrogen sulfide at the oxidation potential of the mediators in the presence of the substrates affords the corresponding aliphatic and aromatic thiols in a yield of 62–75%.

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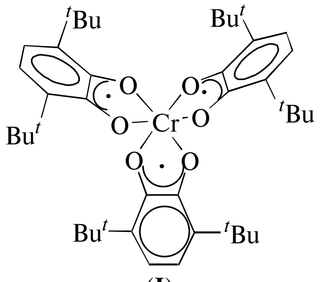
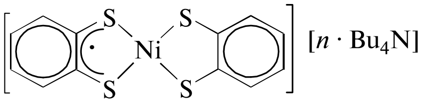
At present the search for new methods of the synthesis of organic compounds is one of the promising directions in organic chemistry. The involvement of electrochemical methods in processes of the oxidative (reductive) transformation of hydrogen sulfide, sulfur, and low-molecular-weight thiols is an actively developed area of organic electrochemistry. Electrochemical transformations of sulfur-containing organic compounds include either the direct generation of their oxidized (reduced) form at the electrode and further reactions in the solvent bulk or the mediator redox process under the action of radical ion intermediates, metal salts, and halogens, which can undergo cyclic regeneration on the electrode. We have earlier shown [1, 2] that the electrochemical oxidation of hydrogen sulfide in the presence of unsaturated compounds affords the sulfur-containing products in a quantitative yield. However, the direct electrochemical method proposed for the synthesis is energy-consuming because of the high anodic potential of oxidation of hydrogen sulfide and thiols. Organic mediators based on substituted triarylamines and phosphines recommended themselves as mediators of the oxidation of hydrogen sulfide and thiols in nonaqueous media. The use of these compounds made it possible to decrease the potential of electrosynthesis of the sulfur-containing organic compounds by 1.0–0.4 V [3, 4]. Nevertheless, the organic electromediators are not universal and can be removed from the regeneration cycle during the reaction because of the formation of poorly soluble salts, which decreases the yield of the target products. Chemical oxidants (sterically hindered *o*-benzoquinones, *o*-iminobenzoquinones, and related transition metal complexes) can also participate in the oxidation of hydrogen sulfide and thiols due to the inner- or outer-sphere electron transfer, which, in turn, changes the oxidation state of the organic ligands.

The purpose of this work is to study the transition metal complexes as electromediators in the electrosynthesis of organic compounds. The objects of the study were the neutral chromium(III) tris-*o*-semiquinolate complex, $Cr(L^{SQ})_3$ (**I**), where L^{SQ} is 3,6-di-*tert*-butyl-*o*-semiquinone, and the monoanionic paramagnetic nickel(II) complex, $[n\text{-}Bu_4N][Ni(L_S^{SQ})(L_S^{DT})]$ (**II**), where L_S^{SQ} is *o*-thiosemiquinone, and L_S^{DT} is benzene-1,2-dithiolate, containing in one molecule an organic redox-active ligand of the *o*-quinoid type and a transition metal ion inert towards hydrogen sulfide:



(I)



(II)

Hex-1-ene, oct-1-ene, benzene, toluene, and benzoic acid were used as substrates involved in the reactions with the oxidized form of hydrogen sulfide formed during electrolysis in the presence of a mediator.

EXPERIMENTAL

The nickel(II) and chromium(III) complexes were synthesized by described procedures [5, 6]. The oxidation potentials were measured by cyclic voltammetry (CV) in a three-electrode cell with an IPC-pro potentiostat under argon. The working electrode was a stationary glassy carbon (GC) electrode with a diameter of 2 mm, and the auxiliary electrode was a platinum wire (S = 18 mm^2). The reference electrode (Ag/AgCl/KCl) was equipped with a water-proof membrane. The number of electrons transferred during the electrode process was estimated with respect to ferrocene used as a standard. The potential sweep was 0.20 V s^{-1}. The supporting electrolyte was 0.1 M Bu_4NClO_4. Solvents were purified and dehydrated according to known procedures [7, 8]. The concentration of complexes **I** and **II** was 0.001–0.003 mol/L.

Preparative electrolysis was carried out on stationary platinum electrodes (plates with a surface area 700 mm^2) in an undivided three-electrode 100-mL cell. The reference electrode was a saturated silver chloride electrode with the electroconducting water-proof membrane. The supporting electrolyte was n-Bu_4NClO_4, and methylene chloride was used as a solvent. Electrolysis was carried out on a PI-50-1.1 potentiostat. The value of potential on the working electrode was established by 0.10–0.30 V more positive than the oxidation potential of the mediator. The time of microelectrolysis depended on the working concentration of the substance under study ranging, on the average, from 2 to 6 h. After the end of electrolysis, the cell was purged with argon for 1–1.5 h for the maximum removal of hydrogen sulfide. The reaction products were identified by the CV method using standard substances. The obtained mixture was dissolved in hexane to separate the supporting electrolyte. Then the solvent was separated from the reaction products using fractional distillation.

IR spectra were recorded on an FSM 1201 FTIR spectrometer in thin KBr films. Sulfur-containing organic substances were identified by the tables of frequencies in the IR spectra [9]. Hydrogen sulfide was prepared by a described procedure [10]. Quantitative analysis of the initial reaction mixtures and obtained products was performed on a Kristall-Lyuks 2000 gas chromatograph equipped with a flame photometric detector. Separation was carried using a ZB-1 capillary column in the linear temperature-programmed regime: the beginning at 35°C, the rate of temperature increase was 4°C/min, and the end of the program was 280°C. Nitrogen was used as a carrier gas. The sample volume was 0.5 μL. The obtained compounds were identified using standards for chromatography.

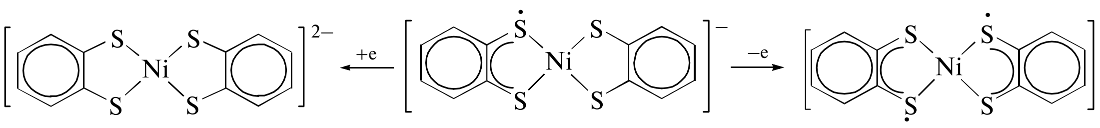
RESULTS AND DISCUSSION

The study of the electrochemical activity of the studied complexes (Table 1) showed that complex **I** containing three o-semiquinone fragments has the completed seven-membered cascade joined by six redox transitions, which corresponds to the change in the oxidation state of the coordinated ligands

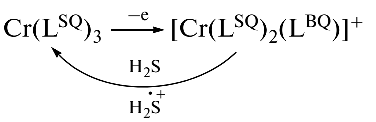
$$\begin{tikzcd}
{[\mathrm{Cr}(\mathrm{L}^{\mathrm{CAT}})_3]^{3-}} \arrow[r, shift left, "-\mathrm{e}"] & {[\mathrm{Cr}(\mathrm{L}^{\mathrm{SQ}})(\mathrm{L}^{\mathrm{CAT}})_2]^{2-}} \arrow[l, shift left, "+\mathrm{e}"] \arrow[r, shift left, "-\mathrm{e}"] & {[\mathrm{Cr}(\mathrm{L}^{\mathrm{SQ}})_2(\mathrm{L}^{\mathrm{CAT}})]^{-}} \arrow[l, shift left, "+\mathrm{e}"] \arrow[r, shift left, "-\mathrm{e}"] & \mathrm{Cr}(\mathrm{L}^{\mathrm{SQ}})_3 \arrow[l, shift left, "+\mathrm{e}"] \arrow[d, shift left, "-\mathrm{e}"] \\
 & {[\mathrm{Cr}(\mathrm{L}^{\mathrm{BQ}})_3]^{3+}} & {[\mathrm{Cr}(\mathrm{L}^{\mathrm{SQ}})(\mathrm{L}^{\mathrm{BQ}})_2]^{2+}} \arrow[l, "-\mathrm{e}"'] & {[\mathrm{Cr}(\mathrm{L}^{\mathrm{SQ}})_2(\mathrm{L}^{\mathrm{BQ}})]^{+}} \arrow[l, "-\mathrm{e}"'] \arrow[u, shift left, "+\mathrm{e}"]
\end{tikzcd}$$

The redox transitions in the cathodic region observed for complex **I** are reversible and one-electron. At the same time, only the first process at the potential $E_{1/2}^{0/1+}$ = 1.02 V is reversible in the anodic region. The further electrochemical oxidation of the chromium complex is irreversible and accompanied by the elimination of free *o*-quinone.

The electrochemical behavior of the monoanionic nickel complex is characterized by two reversible one-electron steps that proceed via the ligands

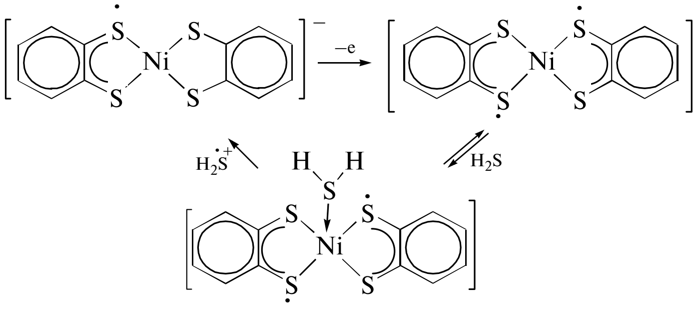


Unlike the earlier considered transition metal complexes with the N,N- and N,S-coordinated redox-active ligands, compounds **I** and **II** are not involved in the oxidation of hydrogen sulfide. In the case of the chromium complex, this is due to steric hindrance of the metal center. In the case of the nickel derivative, this is the monoanionic character. However, for the both complexes the first anodic stage is reversible, which makes it possible to consider these objects as mediators of oxidation. The introduction of hydrogen sulfide in a solution of compound **I** changes the shape of the CV curve (figure): the threefold increase in the current of the first oxidation process is observed in the anodic potential range in the presence of H_2S, and the reversibility of the redox transition disappears. A similar electrochemical pattern is also observed for the nickel(II) derivative. An increase in the current of the oxidation peak indicates the catalytic effect of the complexes [11]. In the case of the chromium compound, the outer-sphere electron transfer from the hydrogen sulfide molecule to the monocation occurs



$$\begin{tikzcd} \mathrm{Cr(L^{SQ})_3} \arrow[r, "-e"] & {[\mathrm{Cr(L^{SQ})_2(L^{BQ})}]^+} \arrow[l, bend left, "\mathrm{H_2S}\ \to\ \mathrm{H_2\dot{S}^+}"] \end{tikzcd}$$

Probably, the inner-sphere mechanism of hydrogen sulfide activation takes place for the oxidized form of complex **II**, which is the coordination of H_2S on the metal center followed by the inner-sphere electron transfer in the $H_2S–Ni–L_S^{SQ}$ system



For the studied complexes **I** and **II**, we calculated the values of decreasing the energy barrier ΔE ($\Delta E = E_R - E_{Med}$, where E_R is the oxidation potential of hydrogen sulfide (1.60 V), and E_{Med} is the potential of the first anodic process of the complexes) of the reaction with hydrogen sulfide: 0.58 (**I**) and 1.12 V (**II**).

To confirm the efficiency of the mediators, we considered the electrochemical activation of hydrogen sulfide by the oxidized forms of complexes **I** and **II** in the presence of unsaturated (hex-1-ene, oct-1-ene) and aromatic (benzene, toluene, benzoic acid) compounds under the electrolysis conditions. The values of the maintained electrolysis potential for complexes **I** and **II** were 1.1 and 0.6 V, respectively. As a result of electrolysis at the potential of mediator oxidation, the corresponding aliphatic and aromatic thiols were formed (Table 2).

It was shown for the reaction of the oxidized form of the $Cr(L^{SQ})_3$ complex with H_2S in the presence of hex-1-ene that the yield of hexane-1-thiol reached 22% within 1 h. An increase in the reaction time (3 h) allows one to enhance the yield of the product to 63%, and the further occurrence of the reaction leads to the accumulation of the products of thiol oxidation (disulfides) in the solution. Similar regularities were established for the most part of the substrates considered. As follows from Table 2, the efficiency of the action of the oxidized form of complex **II** in the reactions with hydrogen sulfide upon the introduction of the substrates into the solution is higher than that for complex **I**, and the yield of the reaction products is 5–10% higher in the case of complex **II**. The mechanism of thiol formation using toluene as an example can be presented as follows:

Table 1. Oxidation potentials (V) of complexes **I** and **II** according to the CV data*

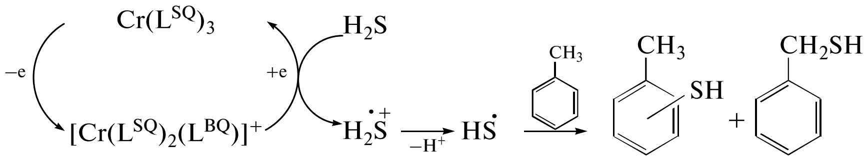
Complex	$E_{1/2}^{2-/3-}$	$E_{1/2}^{2-/1-}$	$E_{1/2}^{1-/0}$	$E_{1/2}^{0/1+}$	$E_{p}^{1+/2+}$	$E_{p}^{2+/3+}$
I	–1.32	–0.86	–0.24	1.02	1.24	1.52
II		–0.46	0.48			

* GC is the glassy carbon electrode, CH_2Cl_2, $V = 0.2$ V/s, 0.1 M n-Bu_4NClO_4, $c = 3 \times 10^{-3}$ mol/L, Ar, vs. Ag/AgCl/KCl (saturated); $E_{1/2}$ is the potential of the reduction and oxidation half-waves; and E_p is the oxidation peak potential.

Table 2. Yields of the reaction products upon the reactions of the oxidized form of H_2S with the unsaturated and aromatic substrates in the presence of metal complex mediators **I** and **II***

Substrate	Total yield of isomeric thiols, %	
	I	**II**
Hex-1-ene	62.0	73.0
Oct-1-ene	63.0	68.0
Benzene	71.0	74.0
Toluene	70.3	75.0
Benzoic acid	70.0	74.3

* CH_2Cl_2, Pt anode, 0.1 M n-Bu_4NClO_4, Ag/AgCl/KCl, $c_{Med} = 0.005$ mol/L, $c_{H_2S} = 0.01$ mol/L, $c_{substrate} = 0.1$ mol/L, and $\tau = 3$ h.



Thus, the principal possibility of using the $Cr(L^{SQ})_3$ and $[n\text{-}Bu_4N][Ni(L_S^{SQ})(L_S^{DT})]$ complexes as electromediators of hydrogen sulfide oxidation was shown and the reactions of the oxidized form of hydrogen sulfide with a series of unsaturated and aromatic substrates affording thiols were carried out.

ACKNOWLEDGMENTS

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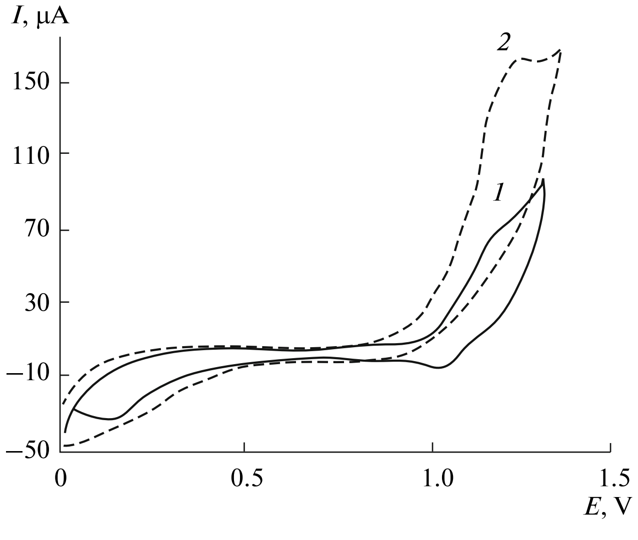

Cyclic voltammogram of the oxidation of complex **I** (*1*) in the absence and in the presence (*2*) of H_2S (1 : 1).

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