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Oxidative Properties of [1,2-*b*]Selenophenes and 4*H*-Selenochromenes and Their Interaction with Hydrogen Sulfide

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Abstract—Electrochemical behavior of [1,2-*b*]selenophenes and 4*H*-selenochromenes in organic media and their interaction with hydrogen sulfide have been studied. In aprotic solvents (CH_2Cl_2 and CH_3CN), the organoselenium compounds are oxidized at anode to give cation-radicals. In the presence of hydrogen sulfide, at its oxidation potential (1.60 V) [1,2-*b*]selenophenes and 4*H*-selenochromenes undergo recyclization into corresponding thiophenes and thiochromenes. The recyclization yielding sulfur analogs have been studied in the presence of organic electromediators, including the transition metal complex with redox-active ligands, as well.

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In recent decades, chemistry of organoselenium compounds has been actively developed due to their unique properties stipulating for numerous applications in many scientific and industrial fields. In particular, organoselenium compounds are used in preparation of chalcogen-containing semiconductors [1, 2] and optical materials [3], and as oxidizers and catalysts [4]. Peculiar biological activity of selenium compounds is another reason of emerging interest to them. Previously, selenium compounds were considered toxic; however, it has been found that selenium is an extremely important ultramicroelement: its deficiency causes serious human and animal diseases. Therefore, selenium-containing heterocyclic compounds form a class of promising veterinary drugs and medical products.

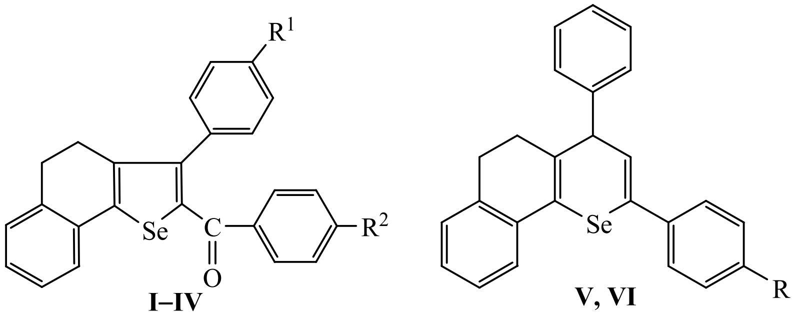
A few works have reported electrochemical studies of selenopyranes in aqueous as well as anhydrous solutions [5, 6]. In particular, selenoxanthene forms selenoxanthenium cation upon electrochemical oxidation in anhydrous medium; in the presence of water, selenoxanthene-9-ol is oxidized into corresponding ketone in several stages [5]. Antioxidant properties of 2,4-diphenyl-7,8-benzo-5,6-dihydro-4*H*-selenochromene and 2-*para*-chlorophenyl-4-phenyl-7,8-benzo-5,6-dihydro-4*H*-selenochromene have been reported in [6].

As early as in 1936 it was demonstrated that five- and six-membered heterocycles were capable of reversible heteroatoms (N, O, S, Se, and Si) exchange. In particular, catalytic transformations of pyrrole, furan, thiophene, and selenophene with ammonia, hydrogen sulfide, hydrogen selenide, and water vapor over aluminum oxide have been studied. At 300–400°C furan undergoes recyclization to form thiophene with yield of 32% [7].

Electrochemical studies of selenium-containing heterocycles reactivity are of definite interest to determine the compounds redox activity and predict their properties. Recyclization of selenium heterocycles into corresponding sulfur analogs under conditions of oxidative activation of the both reagents is of special interest: under standard conditions, exchange of Se with S in heterocyclic compounds is thermodynamically unfavorable, whereas in the case of radical intermediates the reaction direction may be changed and lead to recyclization.

First, we studied redox activity of a series of selenium-containing heterocycles: [1,2-*b*]selenophenes **I–IV** and 4*H*-selenochromenes **V** and **VI** by means of cyclic voltammetry (Scheme 1).

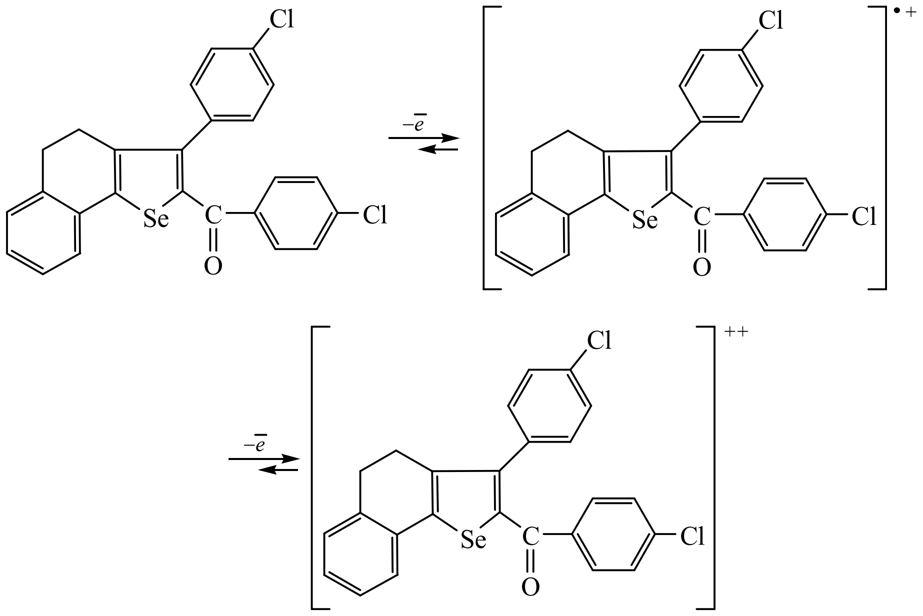
Scheme 1.



I–IV **V, VI**

$R^1 = H, R^2 = H$ (**I**); $R^1 = Cl, R^2 = H$ (**II**); $R^1 = H, R^2 = Cl$ (**III**); $R^1 = Cl, R^2 = Cl$ (**IV**); R = H (**V**); R = Cl (**VI**).

Scheme 2.



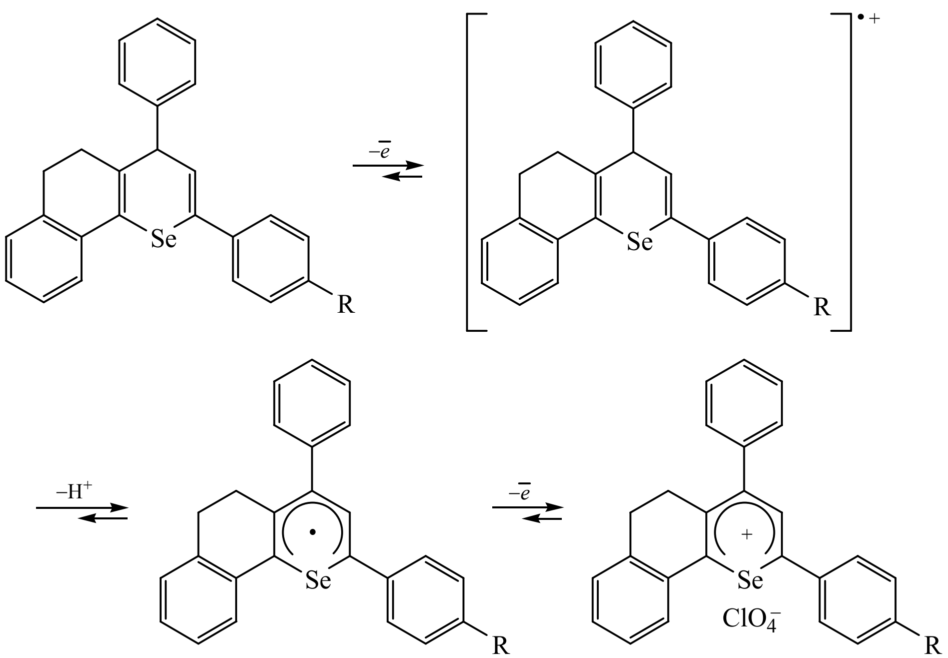
Voltamperograms of compounds **I–VI** revealed two oxidation peaks in the anodic region (Fig. 1 and table).

The tabulated data allowed estimation of the compounds **I–VI** redox activity as function of their structure and the substituent nature. The electron-accepting Cl substituent at R^1 position in the cases of [1,2-*b*]selenophenes **II** and **IV** increased their oxidation potential. Presence of Cl atom at R^2 position did not influence the compound oxidation potential due to the effect of carbonyl group. The six-membered 4*H*-selenochromenes were oxidized easier as compared with the five-membered [1,2-*b*]selenophenes. Basing on the experimentally measured redox potentials, change of acidity of 4*H*-selenochromenes could be demonstrated. Position of the Brønsted–Lowry acid-base equilibrium was estimated taking advantage of the Bordwell equation [8]; in the case of 4*H*-selenochromenes, the acid function value increased as compared with that of molecular form of the heterocyclic compounds [(ΔpK_a(**V**) = 2.72 and ΔpK_a(**VI**) = 3.03].

The first peak of compounds **I–VI** oxidation corresponded to formation of the cation-radical, whereas the second peak accompanied formation of the dication (Scheme 2).

Study of redox properties of 4*H*-selenochromenes **V** and **VI** demonstrated formation of the cation-radical at the first oxidation stage, followed by deprotonation

Scheme 3.



of the cation-radicals to give the selenochromilium radical that was in turn electrochemically oxidized into the selenochromilium cation (Scheme 3).

In the case of [1,2-*b*]selenophene **I**, positions of the absorption bands maxima were changed with time (252, 291, and 355 nm → 268, 355, and 383 nm), and so did the oxidation potentials. The observed changes were due to the compound instability in the presence of air oxygen.

The next stage of the study was devoted to interaction of heterocyclic selenium compounds **I–VI** with hydrogen sulfide. Upon addition of hydrogen sulfide to solution of selenophene **I** in dichloromethane, the yellow solution turned greenish; in the case of compounds **II–VI** the solution color changed from orange to pale yellow. After the interaction, numerous oxidation potentials were not observed any more, and the only oxidation peak was detected at 1.74 V (**I**), 1.82 V (**II**), 1.83 V (**III**), and 1.86 V (**IV**); red shift

Electrochemical and spectral properties of [1,2-*b*]selenophenes **I–IV** and 4*H*-selenochromenes **V** and **VI**[a] (Pt electrode, Ag/AgCl, 0.15 mol/L NBu_4ClO_4, CH_2Cl_2)

Comp. no.	E_{pa1}, V	I_{pc}/I_{pa}	E_{pa2}, V	E_{pc1}, V	E_{pc2}, V	λ_1, nm	λ_2, nm	λ_3, nm	λ_4, nm
I	1.44	0.50	1.74	0.78	–	252	291	355	–
II	1.50	0.42	1.84	0.86	–	264	282	371	462
III	1.44	0.60	1.64	0.75	–	255	292	354	–
IV	1.51	0.44	1.76	0.90	–	256	335	382	475
V	1.25	0.56	1.57	0.74	–0.13	250	–	387	465
VI	1.30	0.42	1.70	0.85	–0.15	259	–	380	468

[a] E_{pa1}, E_{pa2}, E_{pc1}, and E_{pc2} stand for potentials of oxidation and reduction of [1,2-*b*]selenophenes and 4*H*-selenochromenes; I_{pc}/I_{pa} is ratio of current of cathodic peak to that of anodic peak; λ_1, λ_2, λ_3, and λ_4 are absorption maxima.

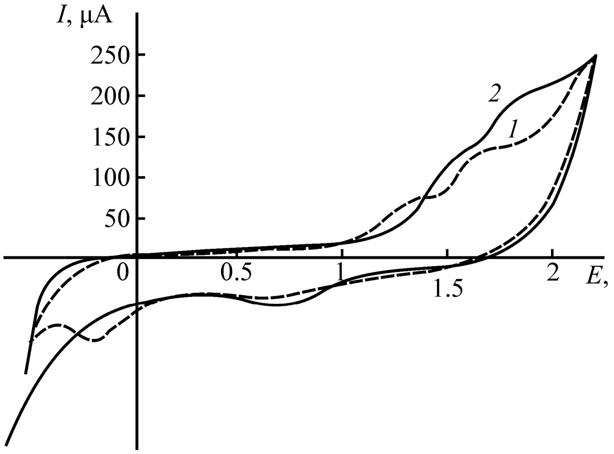
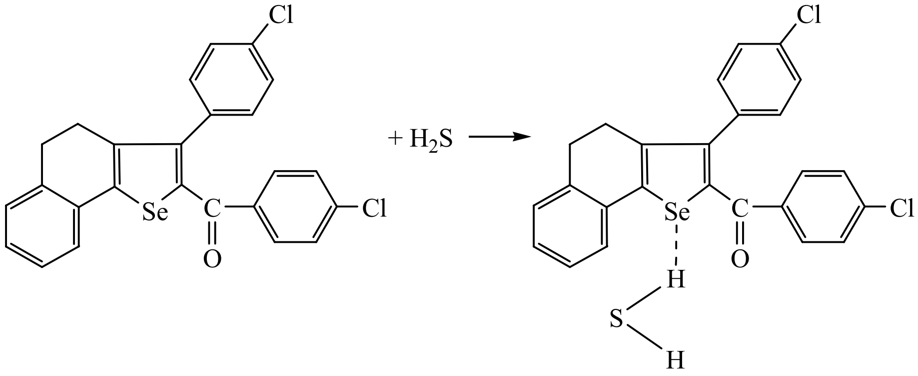


Fig. 1. Cyclic voltamperogram of (*1*) 4*H*-selenochromene **V** and (*2*) [1,2-*b*]selenophene **II** (Pt electrode, Ag/AgCl, 0.15 mol/L NBu_4ClO_4, CH_2Cl_2).

(by about 11 nm) of the electron absorption bands of compounds **I**–**VI** was observed.

It was previously shown [9] that hydrogen sulfide formed the unstable cation-radical upon single-electron oxidation at E_{pa} of 1.6 V ($I_{pc}/I_{pa} = 0$) in aprotic solvents (CH_3CN and CH_2Cl_2). Peak of proton reduction detected in the backwards branch of the voltamperogram at E_{pc} of –0.2 V was assigned using $HClO_4$ as reference; its presence pointed at fragmentation of hydrogen sulfide cation-radical with proton elimination.

Absence of the proton signal in the voltamperogram confirmed formation of adsorption complex between selenophene and hydrogen sulfide with orientation of the latter towards selenium atom (Fig. 2).



Electrolysis of hydrogen sulfide mixture with [1,2-*b*]selenophenes at constant potential of 1.8–1.9 V led to decomposition of the adsorption complex, and new peaks were observed at potentials of 1.54 and 1.80 V (**I**), 1.60 and 1.90 V (**II**), 1.50 and 1.70 V (**III**), and 1.60 and 1.83 V (**IV**). Oxidation potentials of the formed products were shifted towards positive values by 0.1–0.2 V with respect to anodic potential of the initial substrates, due to higher ionization potential of sulfur compared to that of selenium [*I*(S) = 10.36 eV, *I*(Se) = 9.72 eV] [16]. After 3h of electrolysis, yield of [1,2-*b*]thiophenes was of about 24–28%. The electron absorption spectra remained almost unchanged, as Se substitution with S gave the products of structure similar to those of the starting compounds. In the product IR spectrum, the bands at 1615, 1577, and 1497 cm^{-1} were found, typical of thiophene. ^1H NMR spectra of compounds **I**–**IV** contained signals of aromatic (6.9–7.8 ppm) and aliphatic (2.6–3.3 ppm) protons. The electrolysis products ^1H NMR spectra contained similar signals (7.18–7.94 ppm and 2.88–2.95 ppm), thus confirming formation of the sulfur analogs of the starting selenium-containing substrates (Scheme 4).

In [8] it was stated that furan recyclization into thiophene at elevated temperature (300–400°C) proceeded via furan cycle opening at C–O bonds and addition of hydrogen sulfide with subsequent dehydration of the oxythiocompound followed by ring closure at sulfur atom. Under conditions of catalysis with inorganic acids, recyclization was possible at 25–80°C; in that case, homogeneous recyclization occurred via furan ring protonation [10].

With oxidative initiation of the studied reactions, single-electron oxidation of both [1,2-*b*]selenophene and hydrogen sulfide occurred. As was mentioned above, oxidative activation of H_2S (anodic or with single-electron oxidant) gave the unstable cation-radical that further decomposed via deprotonation [11, 12]. Hence, oxidative recyclization of 4*H*-selenochromenes and [1,2-*b*]selenophenes could have occurred via two routes: protonation of the cycle at heteroatom with the product of hydrogen sulfide

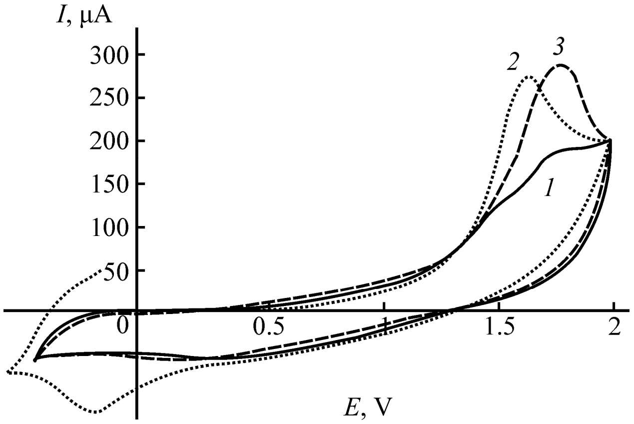
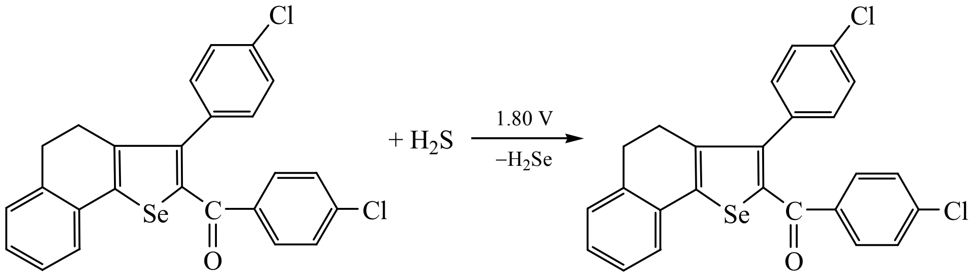


Fig. 2. Cyclic voltamperogram of (*1*) [1,2-*b*]selenophene **IV**; (*2*) hydrogen sulfide, and (*3*) the adsorption complex (Pt electrode, Ag/AgCl, 0.15 mol/L NBu_4ClO_4, CH_2Cl_2).

Scheme 4.



cation-radical fragmentation, or rupture of fairly labile C–Se bond. Activation of the [1,2-*b*]selenophene–hydrogen sulfide mixture could yield the sulfur-substituted derivatives of selenium compounds via attack of thiyl radical at the benzene substituent (the radical being formed in the course of fragmentation of hydrogen sulfide cation-radicals) [13]. Quantum-chemical simulation revealed that radical substitution of Cl with SH was thermodynamically favorable (E_f = –35 kJ/mol).

Further, we investigated activation of the [1,2-*b*]selenophene–hydrogen sulfide system with various electromediators and oxidizers, allowing more efficient oxidation from the consumed energy point of view. Oxidation potential of the electromediator was lower than that of hydrogen sulfide; hence, anodic overvoltage of the electrochemical process was decreased. As the lowest oxidation potential of the studied selenium compounds **I**–**VI** was of 1.25 V, we used the following electromediators: *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (E_{pa} = 0.20 and 0.80 V), tri-*p*-tolylamine (E_{pa} = 0.84 V) and tri-*p*-bromophenylamine (E_{pa} = 1.3 V).

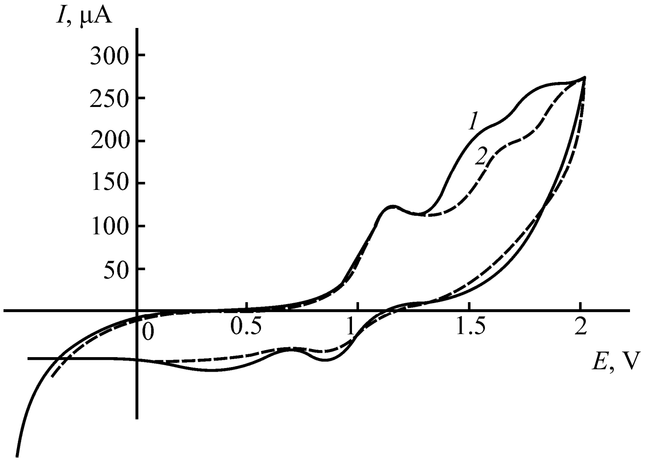
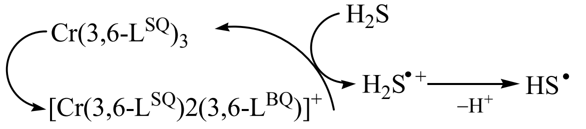


Fig. 3. Cyclic voltamperogram of (*1*) [1,2-*b*]selenophene **IV** in the presence of tri-*p*-bromophenylamine and (*2*) of products of electrolysis of [1,2-*b*]selenophene **IV** and hydrogen sulfide in the presence of tri-*p*-bromophenylamine (Pt electrode, Ag/AgCl, 0.15 mol/L NBu_4ClO_4, CH_2Cl_2).

Figure 3 shows the detected voltamperograms illustrating steady decrease of height of the peak corresponding to reduction of tri-*p*-bromophenylamine cation-radical, pointing at fast interaction between the formed cation-radical and hydrogen sulfide. Electron transfer from H_2S molecule to the mediator induced complete reduction of the latter into the starting form; simultaneously, highly reactive hydrogen sulfide cation-radicals were formed.

Novel mediator was tested in oxidation of the selenium-containing compounds: chromium tris-*o*-semiquinolate Cr(3,6-L^{SQ})$_3$. Single-electron oxidation of one of its ligands gave the active benzoqiunoid form ($E_{1/2}$ = 1.0 V), capable of oxidizing hydrogen sulfide with simultaneous regeneration of the starting tris-*o*-semiquinolate form. The redox processes occurred exclusively at the complex ligands, oxidation state of Cr(III) being unchanged.



Subsequent interaction of the activated hydrogen sulfide with selenium-containing compounds proceeded similarly to the case of electrochemical activation. As a result, products of compounds **I**–**VI** recyclization into their sulfur analogs were obtained.

To conclude, in this work we studied the some structure–property relationships in the series of [1,2-*b*]-selenophenes and 4*H*-selenochromenes. In the presence of molecular hydrogen sulfide, the studied selenium compounds formed the adsorption complex. Oxidation of [1,2-*b*]selenophenes occurred via two electrochemical stages. In the case of 4*H*-selenochromenes oxidation, the two electrochemical stages were separated with the chemical one: formation of the cation-radical was followed by deprotonation and further oxidation to selenochromilium cation. Upon electrolysis at potential of hydrogen sulfide oxidation (1.60 V), [1,2-*b*]selenophenes and 4*H*-selenochromenes gave recyclization products: thiophenes and thiochromenes, their yield being of about 24–28% after 3 h. The recyclization could be more efficient in the presence of organic electromediators, including transition metal complex with redox-active ligands.

EXPERIMENTAL

Electrochemical study of compounds **I–VI** was performed in the 2 mL three-electrode membrane-free cell at room temperature. The compounds concentration was of 1×10^{-4}–5×10^{-2} mol/L. The measurements were performed using the VersaSTAT-400 potentiostat. Cyclic voltamperograms were registered at linear timebase of 0.5 V/s with stationary platinum electrodes. The main electrode was disk-shaped (S = 3.14 mm^2), the auxiliary electrode was plate-shaped (S = 70 mm^2), the reference electrode was silver chloride one equipped with electroconductive waterproof membrane. n-$Bu_4N^+ClO_4^-$ (Aldrich 99.99%) was used as background electrolyte. The solvents (dichloromethane and acetonitrile) were purified using common procedures [14]. Hydrogen sulfide was prepared as described in [15] and applied in form of saturated solution in acetonitrile or dichloromethane. Microelectrolysis of the studied selenium compounds and their mixtures with hydrogen sulfide was performed using platinum plate (S = 70 mm^2) as the main electrode. Preparative electrolysis was carried out with stationary platinum electrodes (S = 700 mm^2) in the 100 mL cell. Potential at the main electrode was set to be 0.1–0.2 V higher than the oxidation potential of the first peak of the selenium compounds or of electromediator using the V3-Studio programmer. Microelectrolysis duration depended on the solution concentration (0.5–3 h). At the average, 12–75 C of electricity was passed through the cell in the course of preparative electrolysis; the coulomb efficiency being of 30–50%.

After electrolysis was over, the cell was bubbled with argon during 1–1.5 h in order to remove hydrogen sulfide. Background electrolyte was precipitated with hexane, and the products were isolated by fractional distillation.

The electrolysis products were analyzed by IR spectroscopy (the FSM 1201 instrument, 400–5000 cm^{-1}). The spectra were assigned using the AIST (RIO-DB SDBS) database and the reference tables [16, 17]. Electron absorption spectra of the compounds solution in deaerated solvent (MeCN or CH_2Cl_2) were recorded with the SF-103 spectrophotometer (190–1100 nm, quartz cell, l of 10 mm, 298 K). ^{1}H NMR spectra were registered with the NB System Varian spectrometer at 400 MHz. Thermodynamic parameters of the reaction were simulated using the PM3 semiempirical method (Gamess).

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