Redox Activation of Hydrogen Sulfide, Thiols, and Sulfur in Electrosynthesis of Organic Di- and Polysulfides

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Abstract—A novel and efficient method for the synthesis of biologically active organic di-, tri- and tetrasulfides has been proposed. Different methods of redox activation of sulfur, hydrogen sulfide, and thiols in the reactions with organic compounds have been considered. Electrochemical initiation of the reactions of the mediator– H_2S-S_8 system with cyclohexane, methylcyclohexane, and benzene has occurred to the formation of polysulfides R_2S_n (n = 2-4). The application of tetrabutylammonium bromide as a mediator of H_2S oxidation has allowed to decrease the anodic overpotential of electrosynthesis. Di- and tetrasulfides have been obtained under anodic activation of the cycloalkanethiols (C_5 , C_6) or thiophenol in the reaction with sulfur. Electroreduction of S_8 in the presence of the same thiols has favored the formation of di- and trisulfides. The yield and the ratio of the R_2S_n (n = 2-4) depend on the method of redox activation of the thiolating reagent.

Keywords: electrosynthesis, organic polysulfides, hydrogen sulfide, cycloalkanethiols, elemental sulfur, redox activation

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Organic di- and polysulfides are widely used in various fields of industry, especially in food and pharmaceutical industry, as potential antifungal, antibacterial, and antitumor compounds [1-4]. Polysulfides R_2S_n (n = 2-4) are platform compounds to design drug molecules. High biological activity of organic polysulfides is related to the possibility of the H₂S formation. Therefore these compounds are often used as a promising source of the endogenous hydrogen sulfide (pro-drugs). Recently, hydrogen sulfide has been recognized as a biologically important molecule involved in various physiological processes [5, 6]. Recent studies have revealed the ability of hydrogen sulfide to actively participate in the signal transmission between the cells in living organisms and to regulate some processes; hence, it can be considered a gas transmitter [7]. One of priority directions in the chemistry of natural and synthetic compounds is the development of novel approaches to the synthesis of compounds acting as hydrogen sulfide donors. Interestingly, there is a correlation between the structure of R_2S_n and the rate of evolution of H_2S via decomposition of organic polysulfides, which should be considered in the design of drugs. Therefore, development of efficient ap-proaches to the synthesis

of di-, tri-, and tetrasulfides with various substituents is an topical issue.

As far as the design of biologically active organic sulfur compounds is concerned, special attention has been paid to the methods of the C-S and S-S bonds formation [8, 9]. The thiolation reactions proceed via the activation of the $C(sp^3)$ -H bond catalyzed by metalcontaining compounds [10, 11] or di-tert-butylperoxide radical initiation [12-14]. Organic tri- and tetrasulfides have been also prepared via the reaction of alkyl(aryl)thiols with sulfur dichloride in the presence of bases in nonpolar solvents [15]. Many successful examples of the synthesis of di- and polysulfides have been reported under the conditions of thermal activation of sulfur have been reported. For example, symmetrical polysulfides have been formed in the reaction of sulfur with diallyl disulfide at the temperature of S₈ melting (115–120°C) [16]. Thermal activation of the S₈-H₂S system at 120-180°C is efficient in the synthesis of organosulfur compounds due to generation of hydropolysulfide and thivl radicals in the melt [17, 18]. Also, the electrochemical method for the preparation of a mixture of organic sulfides R_2S_n (n = 2-4) at room temperature is known,

based on the reaction of alkyl(aryl)thiols with anodegenerated sulfur dication (2.2 V) [19].

We have earlier proposed an electrochemical method of the preparation of R_2S_n (n = 2-4) based on the reaction of C_5 - C_8 cycloalkanes with hydrogen sulfide under the conditions of direct (anode/cathode) activation of H₂S at room temperature and atmospheric pressure [20, 21]. In order to decrease the anodic overpotential of the electrosynthesis, we have also taken advantage of indirect activation of hydrogen sulfide in the presence of Bu₄NBr as mediator of H₂S oxidation [22, 23]. The efficacy of tetrabutylammonium bromide is due to its inertness with respect to the reagent and its ability to oxidation at lower potentials as well as the possibility of regeneration at the cathode [24]. Different methods of H_2S activation in the reaction with cycloalkanes (C_5-C_8) led initially to the products of ring thiolation (cycloalkanethiols and disulfides). The increase in the time of electrosynthesis has promoted the forma-tion of inorganic polysulfanes and sulfur, which are involved in the synthesis of triand tetrasulfides of symmetrical structure [25]. Hence, the earlier per-formed studies have shown that various organosulfur compounds (hydrogen sulfide, thiols, and sulfur) participate in the electrosynthesis of organic di-, tri-, and tetrasulfides. The major advantages of the method are mild conditions and ecological safety of the process. In view of this, the present study aimed to elaborate efficient methods of involvement of organosulfur compounds in the synthesis of biologically active sulfides R_2S_n (n = 2-4) by means of their preliminary redox activation in organic solvent.

Several methods of redox activation of sulfurcontaining reagents (hydrogen sulfide, cyclopentanethiol, cyclohexanethiol, thiophenol, and sulfur) were employed to perform efficient electrosynthesis of polysulfides R_2S_n (n = 2-4). Electromediate oxidation (Bu₄NBr; $E_{ap1} = 0.9$; $E_{ap2} = 1.2$ V) of hydrogen sulfide ($E_{ap} = 1.7$ V) was used to generation radical cation, to reduce the potential of electrosynthesis ($\Delta E = 0.8$ V) in the considered reactions. Generation of the thiyl radical occurred via cyclic transformations of the Br⁻/Br⁻ redox pair at the potential of the first anodic peak. The reaction of the HS radical with S₈ promoted the formation of hydropolysulfide radicals in the solution (Scheme 1).

Dimerization of thiyl radicals as the products of fragmentation of unstable H_2S radical cation favored to the generation of inorganic polysulfanes (H_2S_n) with

Scheme 1.

H₂S
$$\xrightarrow[CH_2Cl_2]{Br} \xrightarrow[Pt]{e} Br}_{E = 1.1 \text{ V}; 25^{\circ}\text{C};}$$
 H₂S $\xrightarrow[H^+]{H^+}$ HS' $\xrightarrow[S_8]{S_8}$ HS'₉

different number of sulfur atoms. Electrolysis at the oxidation potential of the mediator led to the oneelectron oxidation of H_2S_n (0.4–1.5 V) into the HS_n radicals (Scheme 2).

Scheme 2.

$$2HS' \longrightarrow H_2S_2 \xrightarrow{Br \xrightarrow{+e} Br} H_2S_2 \xrightarrow{-e} H_2S_2$$

$$2HS'_2 \longrightarrow H_2S_4$$

Prolonged time of the reaction resulted in the increase of concentration of higher polysulfanes H_2S_n ($n \ge 4-8$), which were converted into S_8 [26, 27]. The Med–H₂S–S₈ system was used for the synthesis of diand polysulfides in the reactions with cyclohexane, methylcyclohexane, and benzene in dichloromethane at room temperature. In the case of cycloalkanes, the corresponding cycloalkanethiols were initially formed (Scheme 3).



Comparative assessment of the reactivity of the thiyl and hydropolysulfide radicals HS_n (n = 2-6) in the reactions with cycloalkanes using quantumchemical calculations showed that abstraction of a hydrogen atom from the substrate under the action of thiyl radical was much easier (by ~75 kJ/mol). Another competiton particle was the bromine radical generated at the anode. However, the mediator concentration in the reaction mixture was much lower than that of hydrogen sulfide, which caused efficient regeneration of Med in the near-electrode layer. Hence, initiation of the reaction with cycloalkanes by thiyl radicals was more probable (Scheme 3).

Cycloalkanethiols RSH formed during the electrolysis were also oxidized by the active form of mediator into cycloalkylthiyl radicals. The generated species are able to dimerize in the near-electrode layer or to react with sulfur in the solution (Scheme 4).

Electromediated oxidation of RSH led to disulfides, whereas unstable cycloalkylhydropoly-sulfides RS_nH were converted into tri- and tetra-sulfides. The process is accompanied by evolution of hydrogen sulfide and sulfur. Polysulfides R₂S_n (n = 2–4) were obtained under the electrolysis of cycloalkanes C₆, C₇ with the Med–H₂S–S₈ system at the oxidation potential of the first anodic peak of the mediator (Table 1). The use of the Med–H₂S–S₈ system allowed reducing of the energy and time costs for the preparation of R₂S_n (n =2–4) as compared to direct anodic activation of H₂S in the presence of S₈.

The total yield of the reaction products obtained from C_6H_{12} and $(CH_3)C_6H_{11}$ grew when the electrolysis time was increased to 2.5 h. The yield of R_2S_n (n = 2-4) was lowered to 24.6 and 37.7%, when the process was carried out during 3 h for cyclohexane and methylcyclohexane, respectively. The concentration of tetrasulfides upon the electrosynthesis was decreased to 14.9 and 20.0%, respectively, likely due to the reaction of R_2S_n (n = 2-4) with H_2S leading to RSH and $RS_{n-1}H$, readily occurring in biological systems [28]. The values of energy effects of the reactions of H_2S with R_2S_n bearing cyclohexyl groups varied from -2.98 to 17.42 kJ/mol. Noteworthily, similar transformations involving low-molecular inorganic sulfanes H_2S_n (n = 2, 3) proceed much easier (ΔH is between -7.75 and 3.77 kJ/mol). The formed unstable intermediate compounds $RS_{n-1}H$ disproportionated into di- and trisulfides with elimination of sulfur. Besides, the presence of bromide ion in the reaction mixture might favor the decomposition of RS_2H into thiols and sulfur [29]. That fact was consistent with the calculated conversion of sulfur, which only slightly varied in the considered reactions (25.8-32.3%). The content of S₈ in the reaction mixture increased when the time of electrosynthesis was elongated, due to the transformation of hydrogen

Table 1. Yield of the products in the reaction of Med–H₂S– S₈ system with cyclohexane and methylcyclohexane under different time of electrosynthesis [$c(S_8) = c(Med) = 5 \text{ mmol/L}$, $E_{el} = 1.10 \text{ V}$, CH₂Cl₂, Pt anode)

	Yield, %				
Value	$C_{6}H_{12}$		$(CH_3)C_6H_{11}$		
	1.5 h	2.5 h	1.5 h	2.5 h	
R_2S_2	5.8	7.2	6.8	9.8	
R_2S_3	4.9	5.7	10.4	11.0	
R_2S_4	16.9	22.6	18.4	25.4	
Σ^{a}	27.6	35.5	35.6	46.2	

^a Σ is the total yield of polysulfides.

sulfides into inorganic polysulfanes. These compounds are able to decompose with the formation of sulfur.

The obtained data revealed higher total yield of di-, tri-, and tetrasulfides in the reaction with methylcyclohexane. The different behavior of this substrate was explained by participation of the thiyl radicals in the reaction at the tertiary carbon atom of the ring. The increase in the yield of polysulfides R_2S_n (n = 2-4) was due to substantial increase in the content of tetrasulfides (Table 1). The ratio of the reaction products was different: R_2S_2 : R_2S_3 : $R_2S_4 = 1.0$: 1.3: 0.6, when electromediated synthesis was performing (1.5 h) in the absence of sulfur in solution. The composition of the reaction mixture was changed in favor of tetrasulfides, hence, the preliminary introduction of sulfur promoted the increase in their concentration. The yield of R_2S_3 in the reaction of cyclohexane with the Med-H₂S-S₈ system was insignificant as compared to that in the case of the methyl derivative. Faster accumulation of disulfides as compared to trisulfides was explained by high rate of dimerization of cycloalkylthiyl radicals. The experi-



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mental data were consistent with the earlier obtained results on direct anodic activation of the H_2S-S_8 system in the reactions with C_5-C_7 cycloalkanes [25].

Besides cyclohexane and its methyl derivative, the transformations of benzene in the presence of the Med- H_2S-S_8 system were investigated under electrolysis conditions at the potential of the first anodic peak of Bu_4NBr (0.9 V). Under those conditions of electrolysis, benzene did not react with activated hydrogen sulfide, since radical substitution reactions are not typical of benzene. Therefore, the electrolysis was performed at the potential of the second oxidation peak of the mediator (1.2 V), which allowed to decrease the anodic overpotential of the hydrogen sulfide oxidation by 0.5 V. As a result, an electrophile (Br⁺) was generated, which attacked hydrogen sulfide That decreased the degree of and benzene. regeneration of the mediator by 15-20% with respect to the transformations of cycloalkanes under similar conditions (95-98%).

The formation of disulfane is occurred in both case of hydrogen sulfide activation at the radical initiation (Scheme 2) or in the interaction with electrophile resulted (Scheme 5).



Under the conditions of two-electron oxidation of bromide ion in the reaction with H_2S , the sulfurcentered cation HS_2^+ was likely generated, which reacted with benzene to afford the intermediate hydrophenyldisulfane (Scheme 6).

The proposed mechanism of electrothiolation of benzene was consistent with the earlier studied electrochemical transformations of aromatic and heterocyclic compounds involving thiocyanogene ions [30, 31]. Electrooxidation of the anion promoted the generation of a reactive intermediate, thiacyanogene (SCN)₂, which attacked the (hetero)aromatic ring to yield the products of thiocyanation [32].

The electrolysis of benzene in the presence of the Med– H_2S-S_8 system for 1.5 h gave the following





mixture of products: $R_2S_2 8.9\%$, $R_2S_3 17.3\%$, and $R_2S_4 31.2\%$. The increase in the reaction duration to 2.5 h led to the increase in the total content of thiolation products to 66.1% ($R_2S_2 11.3\%$, $R_2S_3 18.8\%$, $R_2S_4 36.0\%$), the major contribution to the increased yield being from the tetrasulfides. That fact was explained by the oxidation of unstable hydrophenyldisulfane into R_2S_4 or the interaction with sulfur to give high-molecular polysulfides. As in the case of cycloalkanes, the increase in the electrolysis duration to 3 h did not increase the total yield of the reaction products (52.8%).

As for the preparation of polysulfides R_2S_n (n = 2-4) via electrosynthesis in the absence of a mediator, two approaches were considered: anodic activation of thiols in the reactions with sulfur and cathodic activation of sulfur in the presence of thiols. In the former case, the thiols were oxidized (redox potential for cyclopentanethiol, cyclohexanethiol, and thiophenol was 1.68, 1.72, and 1.75 V, respectively) under the electrolysis conditions (E 1.85 V), while sulfur exhibited higher anodic potential (2.20 V). In the latter case, electrochemical reduction of sulfur proceeded under energetically milder conditions (-1.10; -1.40 V) than cathodic activation of thiols (> -1.80 V). The anodic activation of RSH, as in the presence of mediator (Scheme 4), led to the formation of alkylthiyl radicals reacting with sulfur. Hydropoly-sulfides with high molecular mass (RS₉H) could disproportionate into more stable sulfides R_2S_2 and R_2S_4 (Scheme 7).

Scheme 7.

$$4RS_9H \rightarrow R_2S_2 + R_2S_4 + 3H_2S + 7/8S_8$$

The results of electrosynthesis of polysulfides using anodic activation of thiols in the presence of sulfur are presented in Table 2.

A special feature of that reaction was the predominant yield of tetrasulfides (25.0; 30.5%) as compared to disulfides (16.5; 12.6%) for cyclopentaneand cyclohexanethiol, respectively. However, in case

Table 2. Yield of the products of reaction under anodic activation of RSH in the presence of S_8 [RSH : $S_8 = 2 : 1$, c(RSH) = 20 mmol/L, $E_{el} = 1.85$ V, CH₂Cl₂, $\tau = 1.5$ h, Pt anode]

Compound	Yield of produ	δ, % ^a		
-	R_2S_2	R_2S_4		
<i>cyclo</i> -C ₅ H ₉ SH	16.0	25.4	20.1	
$cyclo-C_6H_{11}SH$	12.3	30.0	33.5	
C ₆ H ₅ SH	27.8	10.1	7.0	

^a δ is the degree of conversion of sulfur.

of thiophenol, the main pathway of the reaction was dimerization of phenylthiyl radicals. Similar features have been observed earlier in the case of the reaction of the electrogenerated sulfur dication with thiophenol [33]. The values of sulfur conversion were consistent with low yield of tetrasulfides caused by low reactivity of phenylthivl radical towards sulfur. Let us note that no trisulfides were formed in the reactions of the studied thiols, due to the absence of sulfur-centered intermediates (HS radical or HS₂ cation) generated from hydrogen sulfide in the reaction mixture. Therefore, when using anodic activation of thiols in the presence of sulfur, hydrocycloalkyl(phenyl)disulfanes which could lead to the formation of trisulfides via disproportionation were not formed (Scheme 8) [28].

Scheme 8.

$2RSSH \rightarrow R_2S_3 + H_2S$

Let us not consider the preparation of R_2S_n (n = 2-4) via cathodic activation of S_8 with thiols. The electrochemical reduction of sulfur is known to yield many reactive intermediates (Scheme 9) [19, 34, 35].

Scheme 9.

$$S_8 \xrightarrow{+2e} S_8^{2-}$$

 $4S_8^{2-} \xrightarrow{} 4S_6^{2-} + S_8$
 $S_6^{2-} \xrightarrow{} 2S_8^{2-}$

Cathodic activation of sulfur in the presence of thiols allowed preparation of a mixture of different polysulfides (Table 3). For cycloalkanethiols, the diand trisulfides were exclusively formed, whereas trisulfides were not detected in the products of the reaction with thiophenol. Such trend was observed in the case of direct anodic activation of thiophenol in the

Table 3. Composition and yield of the products under cathodic activation of S₈ in the presence of RSH [RSH : S₈ = 2 : 1, $c(S_8) = 1.5 \text{ mmol/L}, E_{el} = -1.30 \text{ V}, \text{CH}_2\text{Cl}_2, \tau = 1.5 \text{ h}, \text{Pt anode]}$

Compound	Coulor	\$ 0∕a		
	R_2S_2	R_2S_3	R_2S_4	0, 70
<i>cyclo</i> -C₅H ₉ SH	30.0	29.0	_	42.0
<i>cyclo-</i> С ₆ Н ₁₁ SH	43.0	39.0	—	41.7
C ₆ H ₅ SH	34.6	—	49.0	51.7

 $a^{a} \delta$ is the degree of conversion of sulfur.

presence of sulfur. High concentration of the formed disulfides was due to the reaction of thiols with nucleophilic sulfur species, leading to oxidation of RS anions in the undivided cell (Scheme 10).

Scheme 10.

$$S_8^{2-} + RSH \rightarrow RS_8^- + RS^-$$

 $RS^- \xrightarrow{-e} 2RS^\bullet \longrightarrow R_2S_2$

To obtain R_2S_3 , the HS₃ radicals should be formed in the solution; their recombination with the RS radicals would result in RS₄H. The disproportionation reaction of the latter intermediate compounds would give the trisulfide, hydrogen sulfide, and sulfur (Scheme 11).

Scheme 11. $S_{-}^{-} + RSH \rightarrow HS_{+}^{-} + RS^{-}$

$$HS_{3}^{'} + RSH^{'} \rightarrow RS_{4}H$$
$$2RS_{4}H \rightarrow R_{2}S_{3} + H_{2}S + 1/2S_{8}$$

The formation of tetrasulfides in a rather high yield was observed only in the reaction of thiophenol, in agreement with higher conversion of sulfur. Consequently, the phenylthiyl radical was active towards different polysulfide species formed upon sulfur activation. The advantages of that type of the reaction initiation were the possibility of targeted electrosynthesis of di- and trisulfides and higher conversion of sulfur as compared to anodic activation of cycloalkanethiols. A special feature of that approach was the absence of tetrasulfides in the products of the reaction, since the conditions of anodic activation of sulfur were outside the range of electrooxidation of R_2S_n (n = 2, 3).

In summary, novel efficient approaches for electrosynthesis of di-, tri-, and tetrasulfides using

different methods of activation of sulfur-containing reagents in dichloromethane at room temperature were proposed in this study. The use of the Med $-H_2S-S_8$ redox system in the reactions with cycloalkanes (C_{6} , C_7) and benzene allowed to synthesize R_2S_n (n = 2-4) with the high yield by varying the potential of electrolysis and its duration. Depending on the nature of the substrate, the use of Bu₄NBr as mediator facilitated the decrease in anodic overpotential by 0.5-0.8 V. Activation of H_2S in the presence of S_8 resulted in the generation of thiyl and hydropolysulfide radicals involved in the thiolation reaction. The use of this approach was reasonable for the preparation of tetrasulfides in high yield when di- and trisulfides were present in the mixture of the products. Under the conditions of anodic initiation of the reaction of thiols with sulfur, di- and tetrasulfides were predominantly formed, while thw trisulfides was absent. The cathodic activation of sulfur in the presence of cycloalkanethiols favored the formation of di- and trisulfides; in the reaction with thiophenol, di- and tetrasulfides were obtained. Thus, the method of activation of the used reagent (hydrogen sulfide or thiol) in the presence of sulfur and duration of the reaction were the determining factors in the targeted electrosynthesis of polysulfides. The major advantages of electrosynthesis of R_2S_n (n = 2-4) were mild conditions and high ecological safety of the process.

EXPERIMENTAL

Commercial cyclohexane, methylcyclohexane, benzene, cyclopentanethiol, cyclohexanethiol, thiophenol, tetrabutylammonium bromide (98%, Aldrich), hexane (95%, Alfa Aesar), and sulfur (99.5%, Sigma-Aldrich) were used without purification. Hydrogen sulfide was obtained as described elsewhere [36]. Methylene chloride ("chemical pure") was purified via the known procedure [37]. Bu_4NClO_4 (99%, Acros) was twice crystallized from aqueous EtOH and dried in vacuum during 48 h at 50°C.

Cyclic voltammetry (CV) was used for the analysis of the products mixtures and determination of redox potentials of the compounds. Electrochemical experiments were carried out in a three-electrode cell under argon atmosphere using an IPC-pro potentiostat (working electrode: stationary platinum electrode, 3 mm in diameter; auxiliary electrode: platinum plate, $S = 36 \text{ mm}^2$; reference electrode: Ag/AgCl/KCl with a waterproof diaphragm; potential sweep rate 0.2 V/s; supporting electrolyte: 0.15 M Bu₄NClO₄).

Microelectrolysis of the Med– H_2S-S_8 system (1.5 h) was performed at controlled-potential conditions on platinum electrodes ($S = 30 \text{ mm}^2$) in a diaphragm-free three-electrode cell (2 mL) in dichloromethane at 25°C under argon atmosphere. The concentrations of the mediator (Bu₄NBr) and S₈ was 5 mmol/L; the hydrogen sulfide : hydrocarbon molar ratio equaled 3 : 1, at $c(H_2S) = 30 \text{ mmol/L}$. Hydrogen sulfide was introduced in the reaction mixture after 0.5 h in the form of saturated solution in dichloromethane (20 µL). The concentration of H₂S was determined by gravimetry after the reaction with Pb(CH₃COO)₂. The value of electrolysis potential depended on the nature of the substrate: for cycloalkanes the potential was maintained at 1.10 V (the first peak of oxidation of the mediator), for benzene it was 1.40 V (the second anode peak of the mediator).

Anodic activation of thiols (5 mmol) was performed at controlled-potential conditions at the potential 1.85 V, the RSH : S_8 ratio being 2 : 1 during 1.5 h. Cathodic activation of sulfur (1.5 mmol) was performed at the potential of -1.30 V and the RSH : S_8 ratio of 2 : 1 during 1.5 h.

Large-scale electrolysis (10 mL) of the mixture of hydrocarbons and the Med-H₂S-S₈ system in dichloromethane was performed on platinum electrodes (S =55 mm²) during 1.5 or 2.5 h. The rate of intake of hydrogen sulfide was 2-3 mL/min, providing the required concentration of H₂S in the electrochemical cell. The molar ratio of hydrogen sulfide : cycloalkane was 3 : 1 at $c(H_2S) = 30 \text{ mmol/L}, c(S) = c(Med) =$ 5 mmol/L. The current density was maintained in the range of 5-10 mA/cm² during the electrolysis. After the electrolysis, the reaction mixture was degassed by bubbling argon during 30 min and then concentrated in vacuum. Supporting electrolyte and mediator were precipitated with hexane. The mixture of organic polysulfides was isolated by three-step extraction with hexane, and the extract was concentrated in vacuum.

Large-scale electrolysis (15 mL) with sulfur and thiols was performed at controlled-potential conditions at the potential 1.85 V in dichloromethane on platinum electrodes ($S = 50 \text{ mm}^2$) during 1.5 h. A specimen of sulfur (10 mmol) was preliminarily dissolved in dichloromethane. The solution of sulfur and thiol in the 1 : 2 ratio was deaerated for 5–7 min. For cathodic activation of sulfur in the presence of thiol, the preparative electrolysis was performed at the potential of –1.30 V. The current density was maintained in the

range of 5–10 mA/cm². After the electrolysis, the reaction mixture was concentrated in vacuum. The background electrolyte was precipitated with hexane. The mixture of organic polysulfides and thiols was isolated by three-step extraction with hexane and the extract was concentrated in vacuum.

The obtained organosulfur compounds were identified using the methods of CV, IR spectroscopy, chromatography-mass spectrometry, and X-rav fluorescence analysis. The cyclic voltammograms of the electrolysis products contained three anodic peaks: R_2S_2 (1.50–1.60 V), R_2S_3 (1.73–1.85 V), and R_2S_4 (1.90-2.05 V). In the cases of thiols reactions with sulfur, the peaks of oxidation of the starting thiols were also observed at 1.62-1.75 V. The yield of di- and trisulfides was estimated from the data of chromatomass spectro-metry. In the reactions involving the mediator system, the yield of the electrolysis products was calculated with respect to the reacted hydrogen sulfide, whereas in the case of redox-activation of the RSH-S₈ system, the content of R_2S_2 and R_2S_3 was referenced to the reacted thiol. The yield of tetrasulfides was estimated from the data of CV by determining the ratio between the anodic peaks current of di- and tetrasulfides, taking into account molecular masses of R_2S_n (n = 2, 4) oxidized under those conditions in a single two-electron step. Inorganic polysulfanes (H_2S_n) with different molecular masses were observed by CV method at 0.4-1.5 V. The degree of conversion of sulfur was monitored by means of CV from the decrease in the value of the cathodic peak current (-1.15 V).

IR spectra of the electrolysis products were registered using a FSM-1201 IR Fourier spectrometer (KBr, 400–4000 cm^{-1}). The IR spectra contained the following stretching bands: S-S (507-520 cm⁻¹), C-S $(690-710 \text{ cm}^{-1})$, and S-H (2550-2600 cm⁻¹). The analysis of the mixture of the reaction products was performed by means of GC-MS using a GCMS-QP2010 Ultra instrument (Shimadzu) with massspectrometry detector (EI, 70 eV, SPB-1 SULFUR capillary column (30 m \times 0.32 mm; $t_{\text{max}} = 320^{\circ}$ C, carrier gas: helium, temperature programming of the column from 30 to 280°C). The mass spectra contained the following molecular ions peaks, m/z (I, %): C_5H_9SH : 102 (40) $[M]^+$, 75 (15), 69 (100), 53 (20), 41 (60); $C_6H_{11}SH$: 116 (25) $[M]^+$, 83 (23), 67 (40), 55 (100), 45 (20); C_6H_5SH : 110 (100) $[M]^+$, 84 (14), 77 (12), 66 (31), 51 (10); $(C_5H_9)_2S_2$: 202 (11) $[M]^+$, 134 (21), 69 (100); $(C_5H_9)_2S_3$: 234 (12) $[M]^+$, 101 (25), 67

(55); $(C_6H_{11})_2S_2$: 230 (14) $[M]^+$, 147 (16), 83 (100), 55 (27); $(C_6H_{11})_2S_3$: 262 (16) $[M]^+$, 230 (3), 179 (8), 115 (32), 83 (100), 55 (25); $(C_6H_5)_2S_2$: 218 (100) $[M]^+$, 185 (70), 154 (65), 109 (80), 77 (55), 66 (70); $(C_6H_5)_2S_3$: 250 (8) $[M]^+$, 218 (100), 185 (25), 154 (35), 140 (10), 109 (80), 66 (35); $(C_7H_{13})_2S_2$: 260 (13) $[M]^+$, 163 (17), 130 (10), 97 (100); $(C_7H_{13})_2S_3$: 291 (14) $[M]^+$, 260 (4), 163 (28), 130 (44), 97 (100).

Organic tetrasulfides destruct under the conditions of chromatography-mass spectrometry analysis. In view of that, the mixture of R_2S_n (n = 2-4) was analyzed by means of X-ray fluorescence using an ASE-1 spectrometer to determine the total content of sulfur. The obtained data allowed to calculate the content of R_2S_4 , using the chromato-mass spectrometry data on the yield of di- and trisulfides. The determined yields of tetrasulfides were consistent with the results of electrochemical measurements.

Quantum-chemical calculations were performed using the B3LYP/6-31++G(d,p) density functional method implemented in Hyper Chem 8.0 software. The effect of solvent (CH₂Cl₂) was taken into account by the polarizable continuum model (PCM). The energy effects of the reactions (ΔH) were calculated as the difference of total energies of final and initial structures.

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CONFLICT OF INTERESTS

No conflict of interest was declared by authors.

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