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Electrosynthesis of polysulfides R_2S_n (n=2-4) based on cycloalkanes and S_8 via bromide-mediated oxidation of H_2S

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A new effective electrochemical method of producing organic di-, tri- and tetrasulfides (R_2S_n (n=2-4)) with participation of H_2S, S_8 and cycloalkanes C_5-C_7 in the presence of mediator (*n*-Bu_4NBr) has been developed at room temperature. The activation of H_2S mediated by the redox couple $Br^-/Br\cdot$ in the mixture of S_8 allows to generate simultaneously thiyl and hydropolysulfide radicals leading to formation of polysulfides with different number of sulfur atoms. The mediator decreases the anodic overvoltage of the electrosynthesis of R_2S_n, compared to a direct anodic activation of hydrogen sulfide.

Keywords: organic polysulfides, activation of H_2S, sulfur, cycloalkanes, mediator, electrosynthesis

1. INTRODUCTION

Organic polysulfides are widely used as regulators of natural or synthetic rubber vulcanization, components of lubricating oils, sulfidation chemicals in catalytic reactions, in production of sulfur cement, etc. [1]. Such type of compounds serve as promising compound-platforms for developing pharmaceuticals, such as antidiabetic, anti-inflammatory, antioxidant, cardioprotective, antibacterial and anticancer agents [2-5]. It has been shown that the anticancer activity of diallylpolysulfides grows with increasing the number of sulfur atoms in polysulfide chain [5]. Hydrogen sulfide is one of the gas transmitters that participate in signal transmitting between cells of living organisms [6]. The correlation between structure of polysulfides and the rate of H_2S evolution plays an important role in producing of medicines with prolonged action.

There are different ways of forming C-S, S-S bonds to construct biologically active organosulfur compounds [7]. The introduction of a thioester group occurs to catalytic activation of C(sp^3)-H bond by metal containing compounds [8,9], as well as by initiation of radical reactions of thiolation by di-*tert*-butylperoxide [10,11]. Organic tri- and tetrasulfides are synthesized by the reaction of aromatic thiols with sulfur dichloride in the presence of bases in non-polar solvents [12]. The thermal activation of sulfur is also available method of producing R_2S_n. Symmetrical polysulfides are formed in reaction of diallylsulfide with sulfur at melting point (115-120ºC) [13]. The thermal activation of the mixture of S_8 and H_2S at 120-180°C is also effective in synthesis of various organic derivatives of sulfur [14,15]. This combination of reagents is the sources of the hydropolysulfide and thiyl radicals, which are necessary to create a polysulfide chains. However, the high power consumption and impossibility to regulate the composition of reaction products are serious shortcomings of a thermal synthesis. The alternative method of polysulfides production is electrosynthesis and this approach has considerable advantages over thermal processes. An electrochemical method of obtaining a mixture of organic R_2S_n is particular interest from the position of environmental safety and mild reaction conditions. One of the popular electrochemical methods of producing of R_2S_n (n=2-4) is the interaction of alkyl-, arylthiols with the dication of sulfur at high potential (+2.2V) [16].

Earlier we investigated electrochemical thiolation of cycloalkanes C_5-C_8 by H_2S with formation of thiols and disulfides under room temperature and atmospheric pressure [17-19]. We used different methods of the redox activation of H_2S to an unstable ion-radical form. Organic tri- and tetrasulfides were prepared by method of electrochemical oxidation of H_2S in the reaction with cycloalkanes C_5-C_8 in the presence of S_8. However, this approach is characterized by great power consuming in the course of electrosynthesis [20]. This research is devoted to decrease the anodic overvoltage and to raise the yield of bioactive R_2S_n (n = 2-4) due to using bromide-mediated oxidation of the mixture H_2S with S_8 in the reaction with cycloalkanes.

In this paper, we have proposed to carry out the electrosynthesis of R_2S_n with the participation of cycloalkanes and hydrogen sulfide, which are contained in a rather large amount in oils and gas condensate. The initial compounds show low reactivity in the chemical interactions. The anodic activation of H_2S (+1.8 V) in the presence of S_8 is more favorable than direct electrochemical oxidation of sulfur to dication due to decreasing electrolysis potential to 0.4 V. The oxidation of H_2S by active form of mediator (n-Bu_4NBr) generated at the platinum anode leads to decrease of anodic overpotential to 0.8 V, compared to the direct electrochemical activation of hydrogen sulfide.

2. EXPERIMENTAL PART

2.1. Materials

In this research we used commercially available reagents: cyclopentane, cyclohexane, cycloheptane and methylcyclopentan (98%, «Aldrich»), tetrabutylammonium bromide (98%, «Aldrich»), hexane (95%, «Alfa Aesar»), element sulfur (99.5% «Sigma-Aldrich»), dicyclohexyl disulfide (95%, «Aldrich»), dibutyl disulfide (97%, «Aldrich»), hexyl disulfide («Aldrich»), dipropyl trisulfide (≥95%, «Aldrich») lead(II) acetate trihydrate (>99% «Sigma-Aldrich»), methyl propyl trisulfide (50%, «Aldrich») without additional purification. Hydrogen sulfide was prepared according to the procedure [21]. Purification of dichloromethane was carried out using the known method [22].

2.2. Cyclic voltammetry

The method of cyclic voltammetry (CV) was applied for the analysis of mixture received compounds and the determination of redox potentials. Electrochemical experiments were carried out in a three-electrode cell using a potentiostat «IPC-Pro» under argon. The working electrode was a stationary platinum electrode (d = 3 mm); the auxiliary electrode was a platinum flag (S = 36 mm^2). Electrodes were thoroughly polished and rinsed before and between the measurements. The reference electrode was Ag/AgCl/KCl with watertight diaphragm. The scan rate was 0.2 V/s. The supporting electrolyte 0.15M n-Bu_4NClO_4 (99%, «Acros») was purified as earlier described [23].

2.3. Controlled potential electrolysis

Microelectrolysis of a mixture of H_2S, S_8 and cycloalkane (60-120 min) in the presence of mediator (n-Bu_4NBr, C = 5 mM) performed in an undivided three-electrode cell (2 ml) with platinum electrodes (S = 70 mm^2), at 25°C, in dichloromethane. The molar ratio of hydrogen sulfide : cycloalkane – 3:1 (C(H_2S) = 30 mM), sulfur concentration was 5; 10; 15; 20; 25 mM. Hydrogen sulfide was added as a saturated solution in dichloromethane (20 μl) every 30 minutes. Concentration of H_2S determined by gravimetrical method in the reaction with $Pb(CH_3COO)_2$. The electrolysis at controlled-potential was performed at 1.1 V.

Large-scale electrolysis (10 ml) of cycloalkane with the mixture of H_2S and S_8 in dichloromethane was performed in cell with platinum electrodes (S =70 mm^2) during 120 min. The rate of intake H_2S was 2-3 ml/min, which provided the necessary concentration of H_2S in the electrochemical cell. The molar ratio of hydrogen sulfide : cycloalkane – 3:1 (C(H_2S) = 30 mM), sulfur concentration was 5; 10; 15; 20; 25 mM. The electrolysis at controlled-potential was performed at 1.1 V. The current density was maintained within 5-10 mA/cm^2. The mixture of reaction products was degased by argon (30 min) after electrolysis. The solution was concentrated in vacuum. The supporting electrolyte and mediator (n-Bu_4NBr) were precipitated with hexane. The mixture of thiols (RSH) and polysulfides was extracted by the hexane in three-stage, further the hexane extract was concentrated in vacuum.

CV method, IR spectroscopy, gas chromatography coupled with mass spectrometry (GC-MS), and X-ray fluorescence analysis were used to identify organosulfur compounds.

The cyclic voltammograms of the reaction mixtures after electrolysis shown three well-separated anodic peaks corresponding to the oxidation of organosulfur compounds: R_2S_2 (1.50-1.60 V), R_2S_3 (1.67-1.80 V), R_2S_4 (1.85-2.05 V). The yield of thiols, di-, trisulfides was estimated by GC-MS method. Calculation of the yield of sulfur containing compounds was carried out on the reacted hydrogen sulfide. The concentration tetrasulfides was determined by the CV method. The yield of R_2S_4 was calculated by determining the current ratio of anodic peaks of disulfides and tetrasulfides, taking into account the molecular masses of R_2S_n (n=2,4) capable of two-electron oxidation under these conditions. Inorganic polysulfanes (H_2S_n) with different molecular weights were detected by the CV method in the range of potentials 0.4 - 1.5 V [24]. The sulfur conversion was monitored by changing the current of cathode peak at -1.15 V.

IR spectra were recorded on a FT-IR spectrometer (FSM-1201) in a range of 400 – 4000 cm^{-1}. The valence vibrations of S–S (507-520 cm^{-1}), C–S (690-710 cm^{-1}), S–H (2550-2600 cm^{-1}) bonds were detected in the IR spectra.

Polysulfides were analyzed by GC-MS on a Shimadzu GCMS-QP2010 Ultra instrument with a mass spectrometric detector (ionization method: electron impact, 70 eV). To separate organosulfur compounds capillary column SPB-1 SULFUR (l = 30 m, d = 0.32 mm) was applied. Helium was a carrier gas. The temperature of the column was programmed from 30 to 280°C. The results of mass-spectrometry experiments:

C_5H_9SH (m/z = 102 (M+, 40), 75 (15), 69 (100), 53 (20), 41 (60));
$C_6H_{11}SH$ (m/z = 116 (M+, 25), 83 (23), 67 (40), 55 (100), 45 (20));
$C_7H_{13}SH$ (m/z = 130 (M+, 20), 97 (35), 81 (50), 67 (45), 55 (100));
$(C_5H_9)_2S_2$ (m/z = 202 (M+, 11), 134 (21), 69 (100));
$(C_5H_9)_2S_3$ (m/z = 234 (M+, 12), 101 (25), 67 (55);
$(C_6H_{11})_2S_2$ (m/z = 230 (M+, 14), 147 (16), 83 (100), 55 (27));
$(C_6H_{11})_2S_3$ (m/z = 262 (M+, 16), 230 (3), 179 (8), 115 (32), 83 (100), 55 (25));
$(C_7H_{13})_2S_2$ (m/z = 260 (M+, 13), 163 (17), 130 (10), 97 (100));
$(C_7H_{13})_2S_3$ (m/z = 291 (M+, 14), 260 (4), 163 (28), 130 (44), 97 (100)).

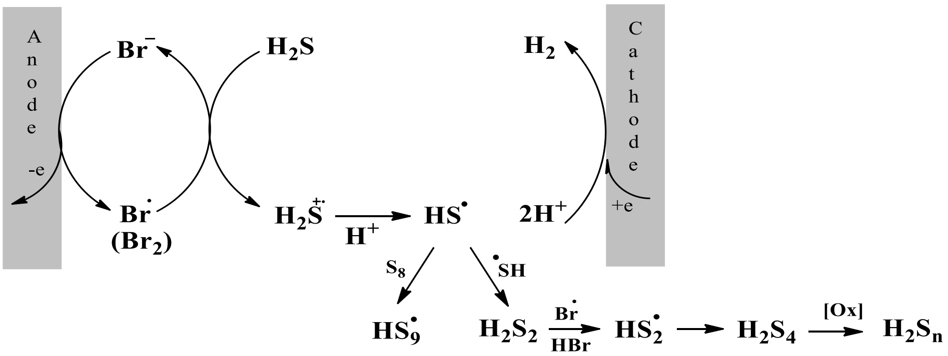
The mass spectra of compounds (R_2S_2, R_2S_3, RSH) forming in the reaction with the participation of methylcyclopentane contain a similar molecular ions as cyclohexane derivatives. Organic tetrasulfides destruct to lower molecular products under GC-MS conditions.

A mixture of R_2S_n (n=2-4) was analyzed by X-ray fluorescence on ASE-1 spectrometer to determinate the total sulfur concentration in the mixture of the reaction products. These data allowed to calculate the percentage of R_2S_4, taking into account the results of GC-MS for R_2S_2 and R_2S_3. The yield of tetrasulfides was correlated with calculations based on the CV method.

Quantum-chemical calculations were carried out in the Hyper Chem 8.0.8 software using the density functional theory (B3LYP/6-31++G(d,p)). Taking into account the effect of solvent (CH_2Cl_2) was carried out using the polarizable continuum model. The energy effects of the studied reactions (ΔH) were calculated as the difference between the total energies of products and initial structures.

3. RESULTS AND DISCUSSION

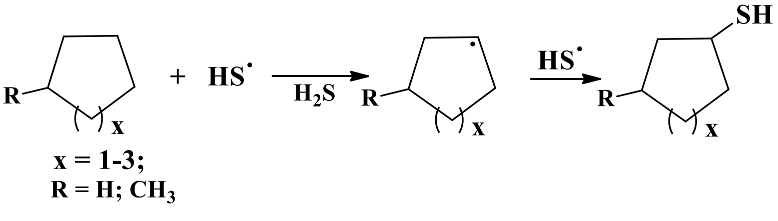
We used two approaches for electrosynthesis of R_2S_n (n=2-4): 1) the application of mediator to decrease potential of H_2S oxidation to the thiyl radical; 2) preliminary introduction of sulfur into the reaction mixture to generate hydropolysulfide radicals. Typically, the active species generated anodically from the halide salts are molecular halogen, halonium ions [25-28]. The mediator has two oxidation peaks at 0.76 V; 1.14 V in CH_2Cl_2. The electrolysis was performed at 0.9 V that leads to generation of bromine atom (or Br_2) at the first oxidation stage of mediator (Scheme 1).



Scheme 1. The scheme of bromide-mediated oxidation of H_2S in the presence of S_8

The excess of H_2S allow to regenerate bromide anion with formation of thyil radical or disulfane. Further the oligomerization of thiyl radicals results in forming of H_2S_n with different number of sulfur atoms, which are oxidized (0.4-1.5V) to HS_n-radicals under electrolysis conditions. Earlier it was shown that the direct anodic activation of hydrogen sulfide lead to formation of inorganic polysulfanes H_2S_n ($n \geq 2$-8) [24]. Under electrolysis conditions polysulfanes were also oxidized by platinum anode and the active form of mediator in the solution (Scheme 1). The polysulfanes with a high molecular weight have a tendency to disproportionate to sulfur and hydrogen sulfide [29]. The process of destruction of H_2S_8 generated during electrochemical reduction of sulfur under acidic conditions was investigated by J. Paris group [30]. Bromide-mediated oxidation of H_2S in the presence of sulfur allows to generate thiyl and hydropolysulfide radicals in solution. In the undivided electrochemical cell the reduction of protons occur on the cathode with generation of hydrogen.

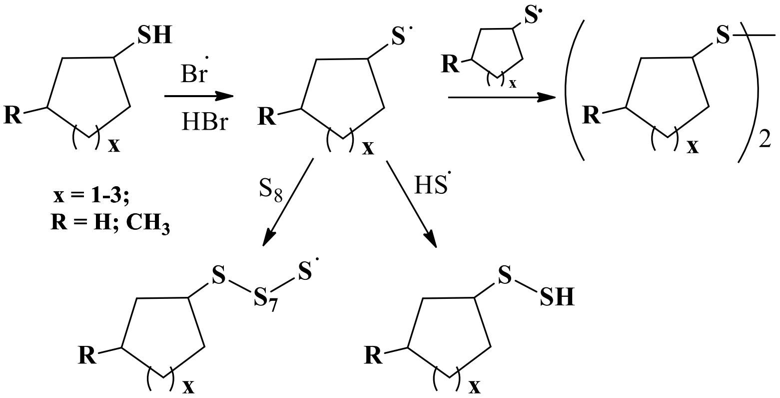
The thiyl radical generated in the first stage of the reaction attacks the carbocycle with formation of cycloalkyl radical. The next step is recombination of two types of radicals which results in cycloalkanethiol (Scheme 2).



Scheme 2. Proposed mechanism of cycloalkanethiols formation

Hydrogen atom transfer activity of HS-radical was recently observed in the reaction of cyclopentane-1,2-diol with hydrogen sulfide at different pHs under photolytical conditions [31]. The thyil radical was generated by one-electron oxidation of HS-anion. The enthalpy of the reaction HS-radical with cyclopentane-1,2-diol is 3 kcal/mol. These data are consistent with our results of the quantum-chemical calculations. The hydrogen atom abstraction from the substrates (cyclopentane, methylcyclopentane) by thiyl radical is also endothermic (8.1 kcal/mol (C_5H_{10}), 5.5 kcal/mol (for tertiary carbon atom in $(CH_3)C_5H_9$)). In the reaction with methylcyclopentane hydropolysulfides radicals ($HS_2^{\cdot}$, $HS_3^{\cdot}$) are not concurrent for HS-radical as the values of thermal effects – 23.0 and 23.6 kcal/mol. At the same time Br-radical can be interact with carbocycle forming cycloalkyl radical. However the concentration of H_2S is higher than the content of mediator, consequently thiyl radical is the main initiator in the reaction with cycloalkanes.

In the course of indirect electrolysis (60 min) of mixture H_2S, S_8 and cycloalkanes C_5-C_7 in the presence of mediator (*n*-Bu_4NBr) there were mainly obtained RSH and R_2S_2, with a low concentration of R_2S_3 (5-10%). The mediated oxidation of cycloalkanethiols leads to cycloalkylthyil radicals. These radicals are able to participate in the reactions with the three different types of sulfur containing particles (Scheme 3).



Scheme 3. Proposed mechanism of disulfides formation

Disulfides generation occurs in result in dimerization of cycloalkylthyil radicals. The reaction is characteristic for these intermediates under electrochemical conditions [32,33]. Other of the reaction pathways can be occurring during the interaction of sulfur with cycloalkyl radical. Similar reaction was considered in the presence of radical initiator, under temperature 120°C, the main product was disulfide [34]. In this research cycloalkylpolysulfide radicals can be the source of different polysulfides (R_2S_n (n=3,4)) as the electrosynthesis is realized at room temperature. Another pathway is the recombination of cycloalkylthyil radicals with thyil radical leading to unstable cycloalkylhydrodisulfides (RSSH). It has known that these compounds have a tendency to destruction to yield mixture of polysulfides and thiols in the reaction with halide ions [35, 36]. Besides, RSSH can interact with disulfides to form trisulfides as the final reaction products [37, 38]. This reactivity of RSSH is explained by the lower value of S – H bond dissociation energy as compared with thiols [39]. Under the electrochemical conditions the oxidation of RSSH (bromide-mediated in the solution or platinum anode) occurs very readily, which favors a high yield of tetrasulfides due to dimerization of RSS-radicals. Such type of reactions is known in the biological systems [38]. The formation of R_2S_n (n=3,4) is also possible due to the interaction of cycloalkyl with hydropolysulfide radicals or sulfur.

It has been shown that disulfides have the oxidation potentials in the range from 1.3 to 1.5 V, trisulfides around 1.6 to 1.8 V, and tetrasulfides around 1.9 to 2.1 V (vs. Hg/HgCl electrode) [40]. The cyclic voltammograms of the reaction mixture H_2S, S_8 and cycloalkanes C_5-C_7 after electrolysis exhibited three well-separated peaks in the range 1.50-1.60, 1.67-1.80, and 1.85-2.05 V (Fig. 1).

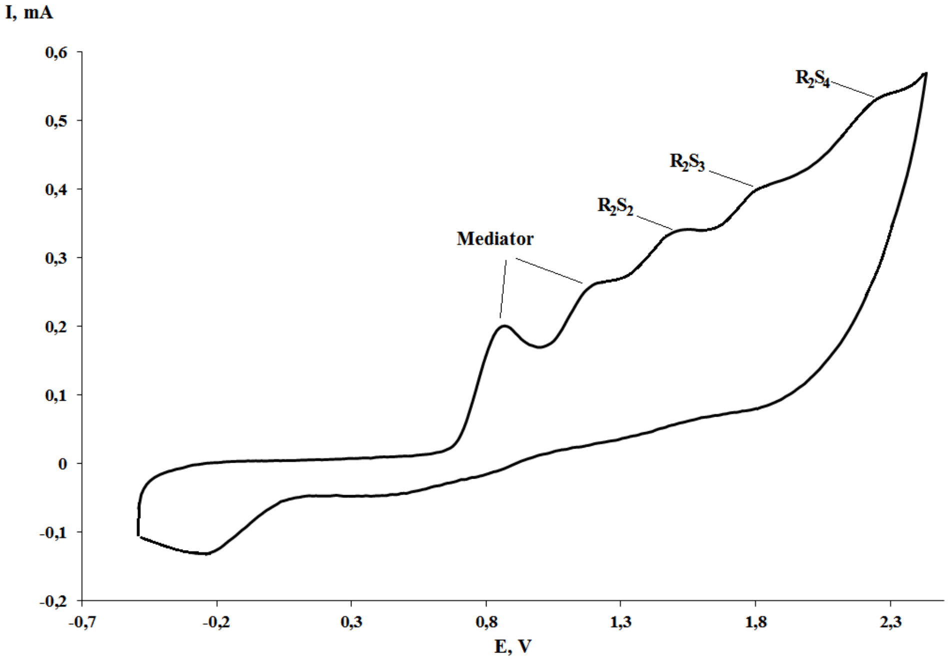
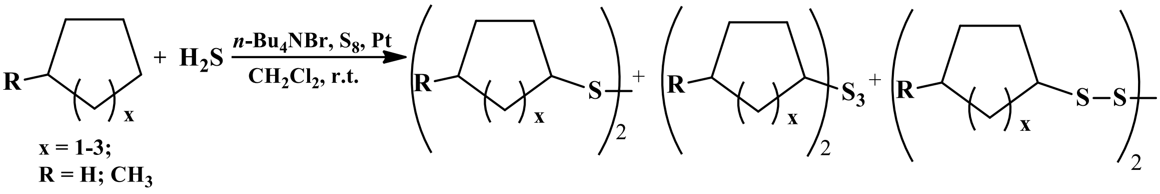


Figure 1. The CV oxidation of polysulfide's mixture after electrolysis of cyclopentane with H_2S and S_8 in the presence of mediator (C(*n*-Bu_4NBr) = 5 mmol, τ=90 min, 1.1 V, Pt-anode, CH_2Cl_2).

Analysis of the CV curves of commercially available di- and trisulfides under similar conditions (Pt-anode, CH_2Cl_2, vs. Ag/AgCl) made it possible to clarify the oxidation potentials of the synthesized compounds. On the example of the compounds: dibutyl-, dihexyl-, dicyclohexyldisulfides shown that the oxidation potential values are 1.47, 1.48 and 1.50 V, respectively. For trisulfides (dipropyl and methylpropyl) the anode potentials are 1.71 and 1.77 V. In CVs we observed that the first and the second anodic peaks correspond to the oxidation of R_2S_2 and R_2S_3, so it is clear that the new peaks at the range from 1.85 to 2.05 V can be attributed to R_2S_4. The potential values correlate with the data from the article [40]. Consequently the value of anodic potential is increased with the length of the polysulfide chain. Therefore cyclic voltammetry is a simple method to determine the composition of mixtures of R_2S_n (n=2-4). The oxidation potentials of these substances shift to anodic area when the numbers of sulfur atoms in polysulfide chain are increased.

The concentration of individual component was determined by measuring the current of the oxidation peaks. Another method to determinate polysulfide concentration in reaction media was the GC-MS. Good reproducibility has been observed in these two methods.

To raise a total yield of R_2S_n (n=2-4) the time of reaction was prolonged up to 90 min. It led to full transformation of cycloalkanethiols into a mixture of di-, tri- and tetrasulfides (Scheme 4).



Scheme 4. The mixture of electrosyntesis products

The introduction of sulfur ($C(S_8)$ = 5 mmol) into the reaction mixture of H_2S with cycloalkane influences the total yield of R_2S_n (n=2-4) at a stationary mediator concentration (Table 1).

Table 1. The influence of sulfur on the yield of R_2S_n (n=2-4) in reaction of cycloalkanes with H_2S in the presence of mediator ($C(n\text{-}Bu_4NBr)$ = 5 mmol, τ=90 min, E =1.1 V, Pt-anode, CH_2Cl_2)

Compounds	The yield of polysulfides, %		
	R_2S_2	R_2S_3	R_2S_4
C_5H_{10}	11.0/24.6	5.2/11.5	16.5/22.0
$(CH_3)C_5H_9$	7.5/14.3	10.1/18.1	10.8/23.9
C_6H_{12}	10.6/16.4	13.9/12.8	6.2/14.7
C_7H_{14}	12.0/10.7	15.8/12.9	20.3/39.5

Notes: $C(S_8)$= 0 / $C(S_8)$ = 5 mmol

All the substrates (C_5H_{10}, $(CH_3)C_5H_9$, C_6H_{12}, C_7H_{14}) showed an increase of total yield of reaction products about 1.2-2.4 times in the presence of S_8. The addition of sulfur prior to electrolysis changes the ratio of the organosulfur compounds: the level of R_2S_4 noticeably increases for cycloalkanes C_6, C_7. The concentration of disulfides doubled in case of C_5H_{10} and $(CH_3)C_5H_9$. Hence, the dimerization of cycloalkylthiyl radicals is prevailed. In the presence of sulfur, the yield of all reaction products is systematically growing in case of $(CH_3)C_5H_9$. This fact can be explained by participation of thiyl radicals in the hydrogen atom abstraction from tertiary carbon atom. In the case of C_7H_{14} the yield of the reaction products proved to be the highest, and for C_6H_{12} it was minimum value. In the presence of mediator the conversion of sulfur in reactions of H_2S with cycloalkanes was approximately 60.0%. This data coincides with the results of anodic activation of H_2S in reactions with cycloalkanes in the presence of S_8 [23]. Thus, the application of a mediator is similar to a direct electrochemical initiation of the reaction, but the feature of this approach is a lower potential of electrolysis.

At the next stage of a research we evaluated the influence of different sulfur concentrations on the total yield of R_2S_n (n=2-4) (Figure 2).

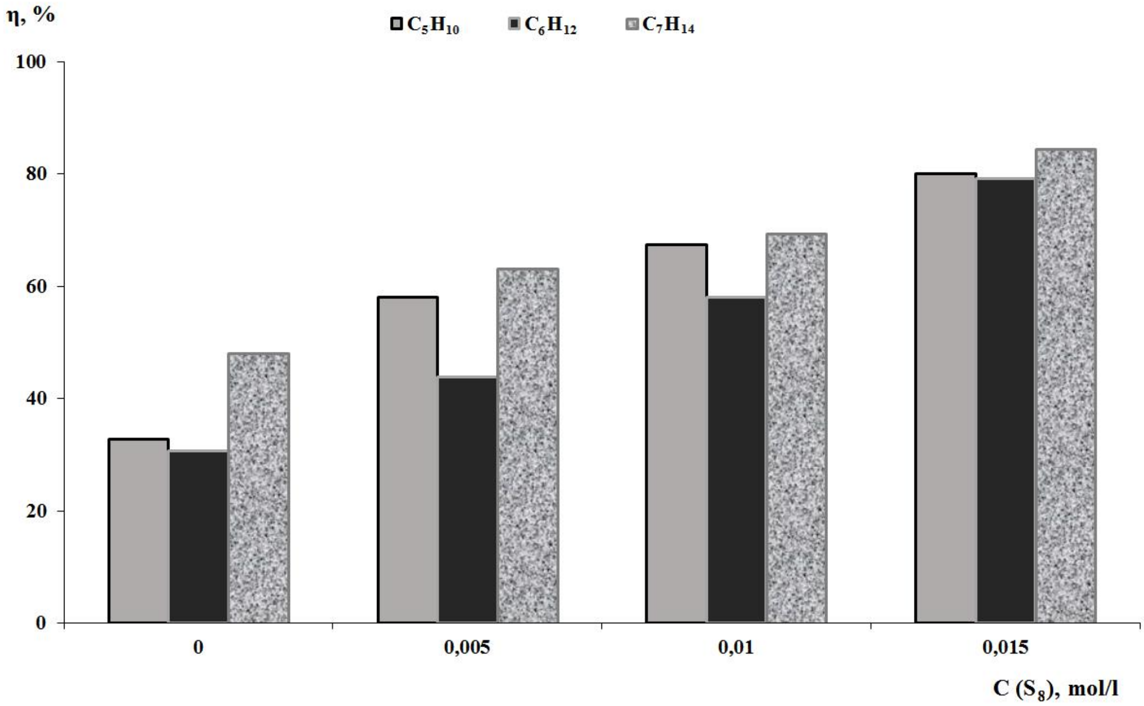


Figure 2. The dependence of polysulfide's total yield (η,%) on sulfur concentration in the reaction of $C_5 - C_7$ with H_2S (1:3) in the presence of mediator (C(*n*-Bu_4NBr) = 5 mmol, τ=90 min, 1.1 V, Pt-anode, CH_2Cl_2).

The total yield of polysulfides for cycloalkanes $C_5 - C_7$ has a linear dependence on the sulfur concentration in the range from 0 to 15 mmol. The greater the size of carbocycle, the greater the total yield of polysulfides (for the equal initial concentration of sulfur). The total yield of R_2S_n (n=2-4) reached maximum at $C(S_8)$ = 15 mmol (79.1 – 84.4 %), which was mainly stipulated by growing content of R_2S_4. The yield of tetrasulfides increased that can be explained by their higher oxidation potential in comparison with di- and trisulfides. In the reaction methylcyclopentane with H_2S and S_8 the content of polysulfides has also linear dependence but the total concentration of R_2S_n increases insignificantly to 65.0%.

Table 2. The yield of polysulfides in the reaction of cycloalkanes C_5-C_7 with H_2S (1:3) (τ = 90 min, C(*n*-Bu_4NBr) = 5 mmol; E = 1.1 V, Pt-anode, CH_2Cl_2)

Compounds	The yield of polysulfides, %		
	R_2S_3	R_2S_4	∑
C_5H_{10}	28.9/28.6	35.5/24.4	80.1/69.5
$(CH_3)C_5H_9$	10.1/11.3	33.9/44.2	65.0/70.7
C_6H_{12}	16.7/16.5	43.8/31.7	79.1/58.9
C_7H_{14}	22.8/20.1	51.7/31.8	84.4/73.0

Notes: $C(S_8)$= 15 mmol / $C(S_8)$ = 25 mmol

An increase of the sulfur concentration to 20 (25) mmol leads to a decrease of the yield of tetrasulfides while the concentration of trisulfides has stationary value (Table 2). This is possible due to the sulfur concentration increasing in the reaction mixture leads to the dominance formation of inorganic polysulfanes. Oxidation of sulfanes to sulfur by two ways (at the anode and the mediator) contributes to the formation of sediment. As a result, the total yield of reaction products decreases.

The optimal sulfur concentration to produce the yield of R_2S_n (n=2-4) was 15 mmol for the studied cycloalkanes. It should be noted that the content of tetrasulfide prevailed over the yield of di- and trisulfides. It has been shown by an example of C_5H_{10} and $(CH_3)C_5H_9$ for the different sulfur concentrations that the yield R_2S_3 depends on the presence of a methyl group in carbocycle. In case of a reaction of C_5H_{10} with H_2S and S_8 to obtain the high yield of trisulfides (28.9%), sulfur concentration is required 15 mmol. The increase of this parameter up to 25 mmol the level of R_2S_3 was practically unchanged.

Thus, we have proposed a method of indirect electrosynthesis of bioactive dicycloalkylpolysulfides R_2S_n (n=2-4) using the mixture of H_2S and S_8 in the reactions with cycloalkanes at room temperature. Electrochemical protocol is an efficient and convenient method to generate thyil and hydropolysulfide via electron transfer between the oxidized form of mediator (*n*-Bu_4NBr) and H_2S in the presence of sulfur. The mediator decreases the anodic overvoltage of the electrosynthesis, compared to anodic activation of H_2S in the presence of sulfur. The primary formed cycloalkanethiols undergo oxidation transformations to disulfides. The intermediate compounds (RSSH) play the main role in the synthesis of trisulfides. The predominant formation of tetrasulfides relates with the participation of sulfur in the radical coupling reactions. The different concentrations of sulfur and the size of carbocycle influence the yield and relation of di-, tri- and tetrasulfides. The environmentally friendly and energy-efficient method developed in this paper has several advantages, such as the use of cheap reagents (hydrogen sulfide, sulfur and cycloalkanes), the absence of initiators of radical nature or metal-containing catalysts.

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