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Thiolation of cycloalkenes C_5, C_6 by redox-activation of hydrogen sulfide

Elena V. Shinkar', Daniil A. Kudryavtsev, Konstantin P. Pashchenko,*
Nadezhda T. Berberova and Alexandra V. Okhlobystina

Astrakhan State Technical University, 414056 Astrakhan, Russian Federation. Fax: +7 8512 614 366;
e-mail: berberova@astu.org

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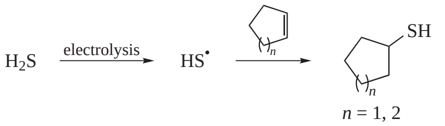
Direct and indirect redox-activation of H_2S in the presence of cyclopentene or cyclohexene in MeCN at 25 °C affords the corresponding cycloalkanethiols.



Direct and indirect redox-activation of poorly reactive substances is a means to improve the efficiency of electrosynthesis of organic compounds under relatively mild conditions.[1,2] The advantages of the electrochemical functionalization of organic compounds include the availability and low cost of the electric current, the possibility of carrying out one-pot synthesis and environmental friendliness of redox process due to the low amount of waste.[3,4] Previously, activation of H_2S was successfully applied to SH-functionalization of alkenes, aromatic and N-, O-, S-containing pentatomic heterocyclic compounds at 25 °C.[5,6]

Cycloalkanethiols are used in production of detergents, polymerization regulators, herbicides and medications (antiseptics, analgesics, antibiotics, *etc*.). They are usually obtained at high temperature, pressure or under irradiation.[7] There are no examples of the electrosynthesis of cycloalkanethiols from cycloalkenes and H_2S at room temperature and atmospheric pressure.

In this work electrochemical reactions of H_2S with cycloalkenes C_5, C_6 were carried out using direct and indirect methods I–VI of redox-activation of H_2S (MeCN, Pt-electrode, Ag/AgCl/KCl as reference electrode) at different electrode potentials (E) (Scheme 1).[†]

$$H_2S \xrightarrow{\text{I–VI}} HS^{\bullet}$$

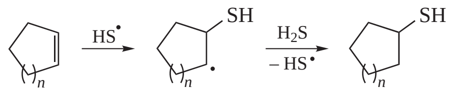
Method of H_2S activation	Pt-electrode	Reactant	E/V
I	Pt-anode		1.6
II	Pt-anode	S_8	1.6
III	Pt-cathode		–1.5
IV	Pt-anode	Q/QH_2	1.1
V	Pt-anode	Bu_4NBr	0.8
VI	Pt-anode	Et_3N	0.1

Q = 3,5-di-*tert*-butyl-*o*-benzoquinone
QH_2 = 3,5-di-*tert*-butylbenzene-1,2-diol

Scheme 1

Cycloalkenes (> 2.3 V) are much more difficult oxidized in MeCN than hydrogen sulfide (1.6 V). Therefore, only reactant undergoes activation during electrolysis of the cycloalkene + H_2S mixture when method I is used. Earlier we established that oxidation of H_2S on Pt-anode in MeCN gives unstable radical cation capable of fragmentation with proton release.[5] The electrochemical data, Bordwell method and quantum chemical calculations revealed the decrease of acidity index (pK_a) as a result of H_2S transformation into radical cation.[9,10] The value of ΔpK_a [$pK_a(H_2S) - pK_a(H_2S^{\bullet+})$] is 18.9.

Electrolysis of cycloalkene **1a**,**b** + H_2S mixtures for 2 h affords cyclopentanethiol **2a** or cyclohexanethiol **2b** (which are oxidized at 1.70 and 1.72 V, respectively) (Scheme 2).



1a,b **a** $n = 1$ **b** $n = 2$ **2a,b**

Scheme 2

During the electrolysis, cycloalkanethiols **2** can undergo oxidation to radical cations, and prolongation of the reaction time (> 2 h) leads to accumulation of dicycloalkyl disulfides **3a**,**b** and dicycloalkyl sulfides **4a**,**b**, whose anodic potentials are 1.56 (C_5), 1.60 (C_6) and 1.86 (C_5), 1.90 V (C_6), respectively (Scheme 3).

The composition of the reaction mixtures was confirmed by cyclic voltammetry, IR spectroscopy and GC/MS.[‡]

In the course of the processes (methods I–VI), along with organosulfur compounds, inorganic sulfanes (H_2S_n, n = 2–8) and sulfur S_8 are formed. In the H_2S–S_8 system generation of thiyl

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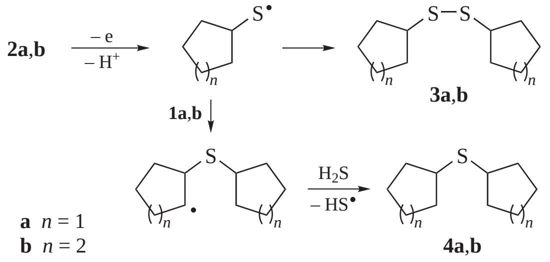
[†] Electrochemical experiment was carried out using an IPC Pro potentiostat. Model reactions and electrolysis of the cycloalkene + H_2S mixture were performed in a one-compartment three-electrode cell (2 ml volume). For the measurement of cyclic voltammograms a working Pt-electrode (a stationary disk, d = 2 mm) was used. The auxiliary electrode was Pt (a plate, S = 70 mm^2). The reference electrode was Ag/AgCl (saturated KCl) with a watertight membrane. The supporting electrolyte was 0.1 M Bu_4NClO_4 (the salt was pre-dried *in vacuo* for 48 h at 50 °C).[8] The potential sweep rate was 0.2 V s^{-1}. The work concentration of cycloalkene and H_2S was 0.005 M.

Preparative electrolysis of the cycloalkene + H_2S mixture was carried out using the PI-50 potentiostat and Pt-electrodes (S = 70 mm^2) at potentials outlined in Scheme 1. The cathodic activation of H_2S was performed in the mode of pulsed electrolysis, the potential sweep range was from 0.5 to –1.7 V. The cycloalkene concentration was 50 mM and the H_2S : **1** molar ratio was 5 : 1. The current density was maintained during the electrolysis as 5–10 mA cm^{-2}. The duration of electrolysis was 2 h. Then the reaction mixture was degassed for 0.25 h in a flow of argon, the supporting electrolyte was precipitated with hexane which also served as extractant of organosulfur compounds. The extraction was repeated three times. The content of organosulfur compounds was controlled using an ASE-1 X-ray fluorescence analyzer. Then the extract was concentrated *in vacuo*.



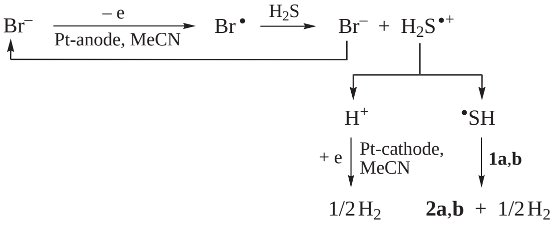
Scheme 3

radicals occurs with high rate thus increasing the yield of organosulfur compounds.[12] Taking this into account, electrochemical transformations of H_2S in the presence of cycloalkenes and sulfur in MeCN were studied. The direct activation of H_2S (method II) was accompanied by the formation of organic polysulfides in 8.1 and 18.8% yields for cyclopentene and cyclohexene, respectively. Thus, the side reaction of radical copolymerization in the presence of sulfur is more typical of cyclohexene.

Cathodic activation of H_2S (method III) was carried out under conditions of pulsed electrolysis at potential sweep in the range from 0.5 to –1.7 V. The H_2S is irreversibly reduced with formation of thiolate anion which is oxidized on anode (0.1 V) to thiyl radical. The direct cathodic activation of H_2S was previously used in reaction of thiolation of cycloheptane at room temperature.[13]

Methods IV, V of redox-activation of H_2S are indirect as they use combined systems containing Pt-anode and chemical reagent (oxidant or electromediator). For activation of H_2S, in method IV Q/QH_2 redox pair was used. Earlier this system was applied in the synthesis of cycloalkanethiols from cycloalkanes C_5–C_8 and H_2S.[14] The first stage of reaction is one-electron chemical oxidation of H_2S by quinone Q with formation of QH_2. The electrolysis of the cycloalkene + H_2S mixture was performed at potential of oxidation of QH_2. It is characterized by the lower value of *E* in comparison with methods I and II.

Carrying out the reaction in the presence of Bu_4NBr using redox pair $Br^-/Br^\bullet$ as electromediator (method V) also allowed us to obtain cycloalkanethiols along with the products of substrate bromination (Scheme 4). At the same time, the decrease in the anodic overpotential (ΔE) as compared with methods II and IV was observed.



Scheme 4

Table 1 Current yields of cycloalkanethiols and anodic overpotentials (ΔE) for reactions of hydrogen sulfide with cycloalkenes C_5, C_6 (t = 2 h).

Method of H_2S activation	Current yield (%)		ΔE/V[a]
	2a	**2b**	
I	28	35	0
II	36	38	0
III	28	35	–
IV	18	23	–0.5
V	29	33	–0.8
VI	39	77	–1.5

[a] ΔE was calculated relatively to the potential of oxidation of H_2S for direct method I.

For indirect generation of thiyl radicals, the combined (Pt-anode + Et_3N) system (method VI) was tested. Earlier this system was used in reactions of SH-functionalization of furan, thiophene and alkenes C_6–C_8 with hydrogen sulfide.[15] In this case the potential of electrolysis significantly decreased due to deprotonation of H_2S with Et_3N. The formed thiolate anion is oxidized on anode to thiyl radical. Under these conditions, the reaction of H_2S with cycloalkenes **1** also affords cycloalkanethiols **2**, disulfides **3** and sulfides **4**.

The current yields of cycloalkanethiols for different methods of redox-activation of H_2S are given in Table 1. In all cases, the yield of cyclohexanethiol **2b** is higher than that of cyclopentanethiol **2a**. The results of electrochemical experiments correlate with the data of quantum-chemical calculations. The calculated values of ΔE_{HF} for the reactions of H_2S with cyclopentene and cyclohexene indicate that the formation of thiols is energetically unhindered (–87.6 and –64.7 kJ mol^{-1}, respectively). As shown above, cycloalkanethiols undergo further transformations. The calculated values of ΔE_{HF} for reactions of dimerization of cyclopentylthiyl and cyclohexylthiyl radicals are –218.7 and –213.8 kJ mol^{-1}, respectively. However, the value of ΔE_{HF} for dicyclopentyl sulfide **4a** formation is significantly lower (–55.0 kJ mol^{-1}) than the corresponding value for dicyclohexyl sulfide **4b** (2.7 kJ mol^{-1}) (see Scheme 3). This difference is probably the main reason for observed lower current yield of cyclopentanethiol.

The current yields of cycloalkanethiols (see Table 1) depend on the method of H_2S redox-activation and, under conditions of activation on electrodes (methods I, III), they are comparable. Replacing the direct method of activation to indirect one is attractive due to lower energy costs for carrying out the electrosynthesis. Meantime, when using electromediators (methods IV, V) the current yield of cycloalkanethiols decreases as a result of side transformations. The combined system including Pt-anode and Et_3N proved to be the most promising, especially in terms of ΔE. In the presence of this combined system, the current yield of cyclohexanethiol **2b** was as high as 77%. However, method VI is characterized by formation of a large amount of elemental sulfur.

In conclusion, the possibility of electrosynthesis of cycloalkanethiols from H_2S and cycloalkenes C_5, C_6 with moderate current yield at room temperature has been demonstrated.

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‡ The GC/MS was performed on a Shimadzu GCMS-QP2010 Ultra instrument equipped with a mass spectrometric detector (EI, 70 eV). A capillary column SPB-1 SULFUR (30 m × 0.32 mm, T_{max} = 320 °C) was used. The carrier gas was helium. The thermostat temperature was programmed from 30 to 280 °C. In mass spectra, the molecular ions of cyclohexanethiol, *m*/*z*: 116.05 $[M]^+$ (calc. for $C_6H_{12}S$, *m*/*z*: 116.07) and cyclopentanethiol, *m*/*z*: 102.05 $[M]^+$ (calc. for $C_5H_{10}S$, *m*/*z*: 102.05) were observed.

IR spectra were obtained in KBr pellets using a FSM-1211 IR Fourier spectrometer. In IR spectra the valence vibrations of S–S (507 cm^{-1}), C–S (690 cm^{-1}) and S–H (2356 cm^{-1}) bonds were detected. Quantum-chemical calculations were carried out in the WinGAMESS 07 software[11] using the density functional theory [B3LYP/6-31++G(d,p)]. The effect of solvent (MeCN) was taken into account using the polarizable continuum model. The energy effects of the studied reactions (ΔE_{HF}) were calculated as the difference between the total HF energies of products and substrates.

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