

LETTERS TO THE EDITOR

Anodic Activation of Hydrogen Sulfide in Reaction with Cyclopentane

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Cyclic thiols are widely used in the synthesis of non-steroidal anti-inflammatory drugs, immunomodulators, antiseptics, soporific, hypoglycemic, and antitumor drugs [1–3]. As a rule, cycloalkanethiols are prepared from cycloalkenes, alcohols, ketones, halogen-substituted cycloalkanes; as a thiolating agent, sulfur, hydrogen sulfide, carbonyl sulfide, or carbon disulfide are applied with the use of photolysis, thermolysis or catalysts [4]. To date, there are no examples of direct methods of thiolation of cycloalkanes with hydrogen sulfide at room temperature.

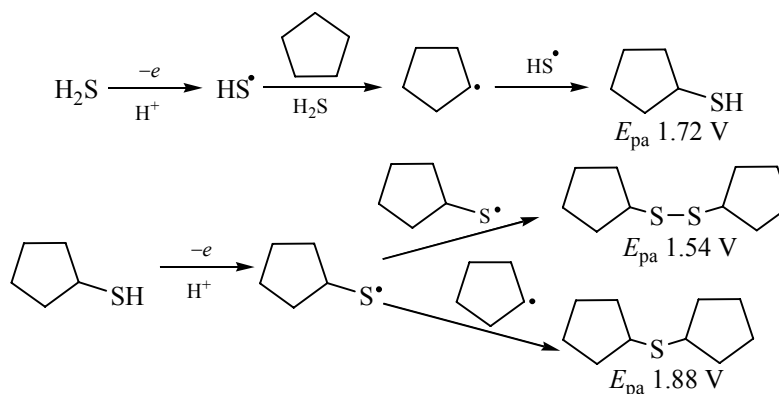
Earlier we have shown that electrochemical activation of hydrogen sulfide on the anode in the presence of organic compounds (benzene, toluene, hexene-1, hexyne-1, furan, thiophene) results in the formation of the products of thiolation of the substrates, as well as the corresponding sulfides and disulfides [5–8]. In order to reduce the energy losses

when performing electrosynthesis of organic sulfur compounds we have successfully used combined redox systems consisting of anode and chemical activator [9–11].

In continuation of these studies, in the present work we have performed the thiolation of cyclopentane, which belongs to fairly inert hydrocarbons, with hydrogen sulfide under the conditions of anodic initiation. As a solvent for electrosynthesis of sulfur-containing derivatives of cyclopentane, dichloromethane was chosen because of poor solubility of the substrate in acetonitrile. The reaction of cyclopentane with H_2S (molar ratio 1 : 5) was performed via microelectrolysis at the reagent oxidation potential during 90 min in anaerobic conditions.

Electrochemical analysis of the products of the reaction by the method of cyclic voltammetry showed the formation of dicyclopentyl disulfide, cyclopentane-

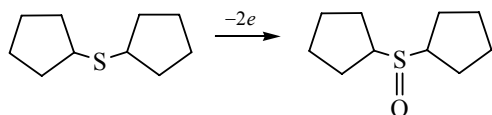
Scheme 1.



thiol, and dicyclopentyl sulfide. The formation of cyclopentanethiol during the electrolysis was independently proved by gas chromatography. The total current yield of organosulfur compounds increases from 15.7 to 49.2% when the time of the reaction increases from 30 to 90 min. A similar dependence is observed for the conversion of the substrate into cyclopentanethiol: 30 min, 12.9%; 60 min, 21.2%; and 90 min, 34.8%. The reaction of cyclopentane with hydrogen sulfide under anodic activation of the reagent can be represented by a series of consecutive-parallel reactions described by Scheme 1.

Taking into account that radical-cation of hydrogen sulfide is unstable and decomposes to proton and thiyl radical, the thiolation of cyclopentane occurs predominantly by the radical substitution mechanism. Cyclopentanethiol formed during the electrosynthesis may undergo single electron oxidation under the conditions of the experiment leading to the formation of cyclopentanethiyl radical. Its transformations into the sulfide occurs with a higher rate than into the disulfide. As a by-product, active sulfur is adsorbed on the surface of the platinum anode, favoring fast accumulation of the sulfide and 1,3-dicyclopentyltrisulfane (2.02 V) [12]. The obtained results are in agreement with those reported in [13], where it has been shown that the unfunctionalization of cycloalkanes with molecular sulfur in superacidic medium also gives rise to the formation of sulfides in high yields (up to 90%).

When performing the reaction of cyclopentane with hydrogen sulfide in aerobic conditions and increasing the time of electrolysis (4 h) and the surface of the electrode (5-fold), the composition of the products was substantially different due to the deep oxidation of the formed organosulfur compounds. Under these conditions, disulfide and sulfoxide are formed as final products (1.96 V):



The mass ratio $(C_5H_{11}S)_2 : (C_5H_{11})_2SO$ was 1 : 1.5. The results of the experiment correlate with the available data on the electrochemical transformations of thiols and disulfides [14]. The composition of the products of the reaction was proved by the methods of IR spectroscopy and high-resolution mass spectrometry. In the IR spectrum, the bands of stretching

vibrations of the following bonds are observed: S–S (507 cm^{-1}), C–S (690 cm^{-1}), and S=O (1021 cm^{-1}). In the mass spectrum, the peaks of molecular ions of dicyclopentyl sulfoxide ($m/z = 186.22$), dicyclopentyl disulfide ($m/z = 202.00$) and 1,3-dicyclopentyltrisulfane ($m/z = 234.01$) are observed.

Therefore, a new electrochemical method for preparation of organosulfur compounds from cyclopentane and hydrogen sulfide by means of anodic activation of the reagent is developed. The elaborated method is an alternative to the known reactions of nucleophilic substitution with participation of halogenated derivatives of hydrocarbons and allows controlling the composition and the yield of the target products.

Electrochemical analysis was performed by the method of cyclic voltammetry in three-electrode cell under an argon atmosphere using potentiostat IPC-Pro. The working electrode was a stationary platinum electrode of 2 mm diameter, the auxiliary electrode was a platinum plate ($S = 60\text{ mm}^2$), the reference electrode (Ag/AgCl/KCl) was with a water-proof diaphragm. The potential sweep rate was 0.2 V s^{-1} . The background electrolyte, $0.1\text{ M Bu}_4\text{NClO}_4$ (+99%, electrochemical grade) was dried in a vacuum for 48 h at 50°C . Methylene chloride (chemically pure) was purified by the known procedure [15]. The concentration of cyclopentanethiol was 5 mmol/L . Microelectrolysis of the mixture ($\text{H}_2\text{S} + \text{cyclopentane}$) was carried out at the hydrogen sulfide oxidation potential (1.8 V) using platinum electrodes ($S = 60\text{ mm}^2$) during 1.5 h in anaerobic conditions (argon). Molar ratio cyclopentane : hydrogen sulfide was 1 : 5.

Preparative electrolysis was carried out in a diaphragm-free three-electrode electrochemical cell using platinum electrodes ($S = 300\text{ mm}^2$) for 4 h in aerobic conditions. Molar ratio substrate : reagent was 1 : 5. The products after preparative electrolysis were isolated in the following way: the reaction mixture was degassed with argon for 2 h; the background electrolyte was precipitated with hexane, which also acted as an extractant of organosulfur compounds; to increase the degree of extraction of the reaction products, three-step extraction with hexane was performed, the extract was concentrated in a vacuum, the content of organosulfur compounds was monitored on a X-ray fluorescent analyzer ASE-1.

For identification of the obtained organosulfur compounds the methods of IR spectroscopy, high-

resolution mass spectrometry, gas chromatography, electrochemistry, and X-ray fluorescent analysis were employed. IR spectra were taken on an IR Fourier spectrometer FSM-1201 in KBr. High-resolution mass spectra were registered on a Bruker Maxis instrument (electrospray ionization, solution in CH₃CN, calibration using HCO₂Na/HCO₂H). Chromatographic analysis of the product mixture was performed on a gas chromatograph Kristallux-4000M (Meta-Chrom Ltd.) in isothermal regime, carrier gas helium, capillary column Agilent (100 m × 0.25 mm), column temperature 80°C, flame ionization detector, temperature of detector 250°C, stationary phase HP-1. Commercial cyclopentane (95%, Alfa Aesar), cyclopentanethiol (97%, Aldrich), hexane (95%, Alfa Aesar) were used without additional purification. Hydrogen sulfide was obtained as described earlier [6].

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