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Binary System Organic Base–Anode in the Oxidative Activation of Hydrogen Sulfide

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Abstract—Initiation of the reaction between hydrogen sulfide and aliphatic, aromatic, and heteroaromatic hydrocarbons in acetonitrile using the binary system organic base–anode is described. The reaction of hydrogen sulfide with nitrogen-containing organic bases is studied by means of cyclic voltammetry. The reaction of hydrogen sulfide with triethylamine leads to the formation of thiolate anion. The next step o reaction is electrochemical oxidation of the thiolate anion that to lead thiyl radical formation *in situ* thiyl radicals. In the presence of binary system on the basis of hydrogen sulfide aliphatic, aromatic, and heteroaromatic thiols and sulfides are formed at room temperature.

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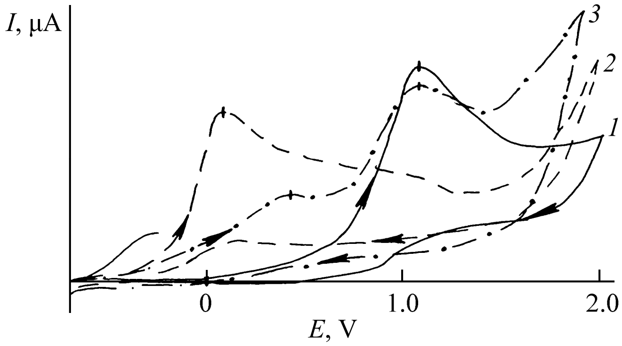
Reaction of hydrogen sulfide with hydrocarbons is traditionally considered from the position homolytic cleavage of S–H bond resulting from thermolysis (400–650°C), radiolysis, photolysis or of ionic mechanism in the presence of mineral acids, acid catalysts, and Lewis acids [1–4]. Previously it was shown that the electrochemical oxidation of hydrogen sulfide (1.6 V) in CH_3CN included the stages of one-electron transfer and subsequent fragmentation of unstable radical cation [5]. The combination of electrochemical and chemical processes (EC) results in the formation of key intermediates, the proton and thyil radical. The generated species take part in ionic and radical reactions with organic compounds simultaneously that lead to the formation of sulfur-containing products at room temperature [6].

In this work we offer to use for the activation of hydrogen sulfide in the reactions with organic compounds a binary "organic base–anode" system combining the advantages of acid-base interaction and the anode initiation. The feature of this system is the changed sequence of stages of hydrogen sulfide activation: the chemical step comes before the electrochemical one (CE).

The aim of the work is the development of effective synthetic method of organosulfur compounds production using the binary "organic base–anode" system. The method permits to decrease significantly the energy consumption necessary to realize the reaction.

In the work a series of organic bases including pyridine **I**, quinoline **II**, acridine **III**, trimethylamine **IV**, triethylamine was considered **V**. It was found that hydrogen sulfide reacted with heterocyclic bases **I–III** to form unstable at-complexes (1.3–1.5 V) detected by cyclic voltammetry. Molecular complexes decompose in air and at heating to 40°C. The formation of pyridinium (–0.64 V), quinolinium (–0.68 V), acridinium (–0.72 V) cation was observed during the electrolysis performed at the potential of at-complex oxidation. In the reaction besides the formation of cations of heterocyclic compounds dimerization of thyil radicals occurred that led to sulfanes. The reaction of bases **I–III** with hydrogen sulfide under the above-mentioned conditions proceeds according to EC mechanism. The bases **I–III** [pK_a (C_5H_5N) 5.14, pK_a (C_9H_7N) 4.85, pK_a ($C_{13}H_9N$) 5.60] insignificantly (on 0.1–0.3 V) decrease the potential of electrolysis. Therefore application of these compounds to decrease the energy consumption in process of thyil radicals generation from hydrogen sulfide is unreasonable.

The compounds **IV, V** exhibit strong basic properties [pK_a (Me_3N) 10.65, pK_a (Et_3N) 9.76] in reactions with H_2S. The introduction of the bases **IV, V** leads to preliminary deprotonation of hydrogen sulfide to result in thiolate anion formation. This intermediate oxidizes at low anodic potential. The



(*1*) Cyclic voltammogram of oxidation of compound **V**; (*2*) after addition of hydrogen sulfide (1:1); (*3*) after electrolysis for 1 h at E_{pa} 0.3 V. (Pt electrode, CH_3CN, 0.1 M NBu_4ClO_4, Ag/AgCl).

process results in the formation of the anode-generated thiyl radical [scheme (1)].

$$H_2S + {:}B \longrightarrow [HB]SH \xrightarrow[-[HB]^+]{-e} HS^\bullet. \qquad (1)$$

Under aerobic conditions the formation of thiolate anion cannot be detected electrochemically because it is unstable in acetonitrile. In the course of the reaction a complete transformation of hydrogen sulfide to elemental sulfur occurs in the presence of bases **IV, V**. Sulfur was identified by the X-ray fluorescent analysis and electrochemical (–0.70 V) methods [7]. This process proceeds through the stage of the formation of lower hydrogen sulfide homologs (H_2S_2) which in the presence of air oxygen undergo disproportionation to sulfur. This fact is in agreement with the low stability of polysulfide anions in the aerated water solutions where the formation of thiosulfate anions is observed [8].

On the cyclic voltammetry curve an irreversible oxidation peak of thiolate anion is observed under anaerobic conditions in the reaction of hydrogen sulfide with bases **IV, V**.

The absence of oxidation peaks of compound **IV, V** on cyclic voltammogram in the range 0.8–1.0 V indicates the complete conversion of bases in the corresponding cations.

The electrolysis under the controlled potential 0.30 V leads to the formation of sulfanes H_2S_4. In the UV spectrum of reaction products absorption bands with λ_{max} 300–320 nm were observed. On the cyclic voltammetry curve an oxidation peak at the potential 0.40 V was registered [1, 8]. In the near-electrode area the dimerization of thiyl radicals takes place with the subsequent oxidation of dimer leading to the growth of polysulfide chain and to the shift of the peak of sulfanes oxidation to the anodic area by 0.2 V [see scheme (2)].

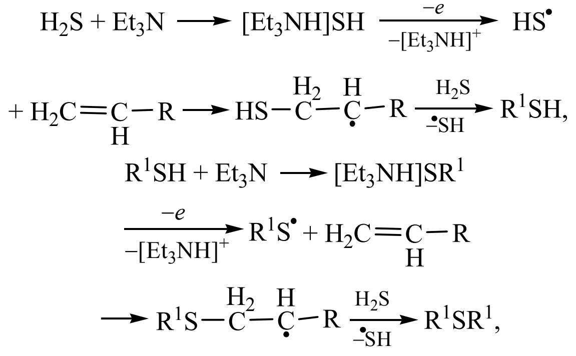
$$HS^- \xrightarrow{-e} HS^\bullet \xrightarrow{HS^\bullet} H_2S_2 \xrightarrow{-e} H_2S_2^{\bullet +}$$
$$\xrightarrow[-H^+]{} HS_2^\bullet \xrightarrow{HS_2^\bullet} H_2S_4. \qquad (2)$$

Due to the synchronic action of the bases **IV, V** and oxidative activation it became possible to generate HS radicals at the decrease in the anodic overvoltage by 1.46 V.

The developed binary system was used to perform electrosyntheses of organosulfur compounds with participation of hydrogen sulfide and hexene-1, toluene, furan, thiophene under the anaerobic conditions. These substrates oxidize at the potentials above 1.8 V (against Ag/AgCl), hence at the potential of performing of electrolysis (0.3 V) only the oxidation of the thiolate anion will occur.

Application of the proposed binary system organic base–anode to activate of hydrogen sulfide according to the CE mechanism permitted to realize the reactions with above-mentioned organic substrates.

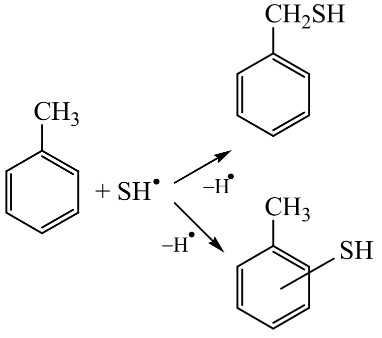
Hexanethiol-1 and sulfanes formed during one hour electrolysis of the hexene-1–H_2S system in the presence of the compound **IV**. Increase time of reaction to two hours led to dihexylsulfide as the product of hexanethyil radical addition to substrate [scheme (3)]. Thiol:sulfide ratio was 2.4:1, the yield of thiol reached 34.6%.



$$H_2S + Et_3N \longrightarrow [Et_3NH]SH \xrightarrow[-[Et_3NH]^+]{-e} HS^\bullet$$
$$+ H_2C{=}\underset{H}{C}{-}R \longrightarrow HS{-}\overset{H_2}{C}{-}\overset{H}{\underset{\bullet}{C}}{-}R \xrightarrow[-{}^\bullet SH]{H_2S} R^1SH,$$
$$R^1SH + Et_3N \longrightarrow [Et_3NH]SR^1$$
$$\xrightarrow[-[Et_3NH]^+]{-e} R^1S^\bullet + H_2C{=}\underset{H}{C}{-}R$$
$$\longrightarrow R^1S{-}\overset{H_2}{C}{-}\overset{H}{\underset{\bullet}{C}}{-}R \xrightarrow[-{}^\bullet SH]{H_2S} R^1SR^1, \qquad (3)$$

$R = –C_4H_9$; $R^1 = –C_6H_{13}$.

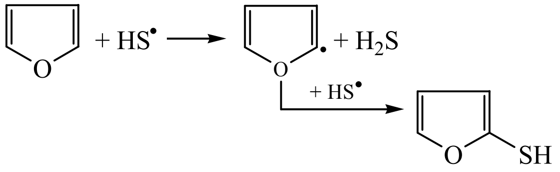
The reaction of toluene with hydrogen sulfide in the presence of compound **IV** leads to a mixture of radical thiosubstitution products of the substrate (37.5%) [see scheme (4)].



(4)

Symmetric aromatic disulfide (20%) and sulfanes (22.2%) were fixed at the increasing of the electrolysis time.

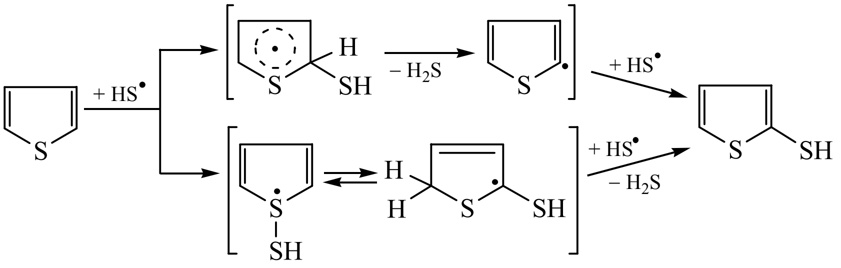
Furan reacts with hydrogen sulfide in the presence of compound **IV** to give 2-furanthiol (29.3%) [see scheme (5)].



(5)

The preliminary stage of deprotonation of hydrogen sulfide with base permits to alter the composition of products as compared to the direct electrochemical initiation of the reaction of hydrogen sulfide with furan [9]. The absence of the product of furan recyclization to thiophene under the conditions described is explained by binding the proton with base **IV**.

Performing thiophene electrolysis with hydrogen sulfide for 1 h in the presence of base **IV** gave 2-thiophenethiol in the first stage [see scheme (6)].



(6)

Increasing the reaction time to 2 h led to the deprotonation of 2-thiophenethiol in the presence of base **IV** and the formation of bis(2-thienyl)sulfide (41.2%) and bis(2-thienyl)disulfide in 3:1 ratio.

Hence, the binary system organic base–anode proved to be effective for performing electrosynthesis of organosulfur compounds on the basis of hydrogen sulfide at room temperature. Main advantages of this system are the decrease in power capacity of generating thiyl radicals from hydrogen sulfide and hence the increase in selectivity of the reactions with their participation.

EXPERIMENTAL

For identification of the compounds synthesized IR spectroscopy, chromatomass spectrometry, gas chromatography, electrochemical methods, and X-ray luminescent analysis were used. IR specra were recorded on a FSM-1201 Fourier spectrometer in KBr pellets. Chromatomass spectral studies were carried out on a Hewlett Packard 5890 instrument equipped with a mass-selective detector and HP-5 capillary column (25 m, SE-30) at the ionization energy 70 eV. The chromatographic analysis was carried out on a Yanaco G3800 gas chromatograph (Japan) equipped with a flame ionization detector, a glass column (3×1500 mm) with a stationary phase 5% SE-30 on Chromaton N-AW-DMCS (0.160–0.200 mm). Column temperature was programmed in the range 20–140°C at a rate 10°C/min, carrier gas helium at a flow rate 20 ml/min. The oxidation potential measurements were carried out by the cyclic voltammetry method in a three-electrode cell under argon with the help of IPC-Pro potentiostate. The operating electrode was the stationary platimun electrode, 2 mm diameter, the auxiliary electrode was the platinum plate (S = 21 mm^2). The reference (Ag/AgCl/KCl) electrode with the waterproof diaphragm was used. Potential sweep rate was 0.2 V s^{-1}. Background electrolyte 0.1 M Bu_4NClO_4 (+99%, electrochemical grade) was dried in a vacuum for 48 h at 50°C. Purification of acetonitrile was carried out according to a known procedure [10]. The concentration of compounds **I–V** was 0.005 M. The exhaustive electrolysis of a hydrogen sulfide–base **IV, V**–substrate mixture was carried out in acetonitrile against the NBu_4ClO_4 background using platinum electrodes (S = 21 mm^2) at the potential of oxidation of thiolate anion 0.3 V. Time of electrolysis 2–3 h. Reagent-base ratio was 3:1. Hydrogen sulfide was obtained according to the procedure described in [11]. Hydrogen sulfide concentration was evaluated gravimetrically and potentiometrically [12]. The identification of elemental sulfur was carried out by the X-ray fluorescent analysis on a scanning VRA-30 spectrometer.

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