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Anodic Initiation of the Hydrogen Sulfide Reactions with the Hydrocarbons of C_nH_{2n-2} Series

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Abstract—We examined the interaction of alkynes and alkadienes with hydrogen sulfide under the conditions of electrochemical initiation of the reaction. One-electron oxidation of hydrogen sulfide leads to the generation of reactive particles (thiyl radical and proton), which react with unsaturated hydrocarbons by two different routes. Hydrogen sulfide acts as a bifunctional reagent forming new C–S bonds, but also exhibits the properties of hydrogenating agent. Varying the experiment duration, reactants ratio, and solvent, it is possible to influence the composition and amount of the formed organic sulfur compounds.

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Interest in the involvement of unsaturated compounds in the reaction with hydrogen sulfide is associated with the ability to obtain a wide range of functional derivatives of sulfur (thiols, sulfides, disulfides), based on a simple and affordable sulfurizing agent, the hydrogen sulfide. Addition of the sulfur-centered intermediates to alkynes is a method of direct production of vinyl sulfides, which are valuable synthons [1] that can be used due to the sensitivity to the attack of both electrophilic and nucleophilic particles.

The principles of nucleophilic addition create a basis for many reactions of the sulfur-containing nucleophiles with olefins and alkynes. The reaction by ionic mechanism occurs only with activated acetylenes in an alkaline medium [2]. Reaction of thiols with unactivated alkynes requires the use of radical initiators, transition metal catalysis, or high temperature. Reactions of sulfurizing agents such as RSSR, RSR, and RSH with terminal alkynes occur by two mechanisms: ionic and radical [3]. The radical addition reactions proceed contrary to the Markovnikov rule to form the adduct of *trans* configuration. With the low-valence transition metal complexes used as catalysts in the reaction of thiols with alkynes these reactions proceed according to Markovnikov rule with the formation of the *cis*-adducts [4]. Reaction of thiols with diene hydro-carbons also occur along the Markovnikov rule, both with and without a catalyst [5].

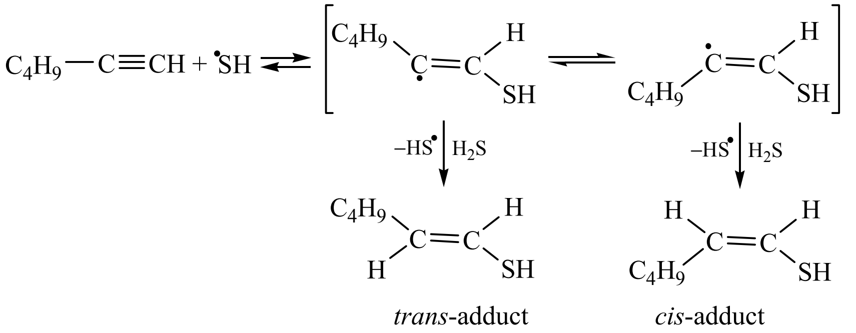
Hydrogen sulfide as sulfurizing agent is used in gas-phase high-temperature reactions with organic compounds, or in liquid-phase processes, when a sulfur–hydrogen sulfide system is used as a source of thiyl radicals [6]. It was shown previously that electrochemical oxidation of hydrogen sulfide led to the formation of radical cations interacting with hydrocarbons, which allowed obtaining various sulfur-containing products [7].

In this paper we consider the interaction of a number of unsaturated hydrocarbons C_nH_{2n-2} with H_2S in terms of electrochemical activation of the latter to produce sulfur-containing functional derivatives.

The reactions of hex-1-yne, hept-1-yne, hex-3-yne, diphenylacetylene, buta-1,3-diene, 2-metylbuta-1,3-diene, and cyclohexene with hydrogen sulfide was carried out under the conditions of electrochemical oxidation of the reagent in aprotic organic solvents. One-electron oxidation of hydrogen sulfide occurs at a potential of 1.6 V, and leads to the generation of the reactive radical cation [8, 9], which decomposes into a proton and thiyl radical ($HS^•$). The latter exhibits electrophilic properties and can be involved in the addition to a multiple bond, abstraction of a hydrogen atom, or dimerization . The study of redox properties of the investigated hydrocarbons showed that they are oxidized at high anodic potentials (E_p > 2.00 V) (see the table).

In order to achieve a high concentration of thiyl radicals in solution which is required for the radical addition [10], we performed electrolysis of a solution containing hydrogen sulfide and an unsaturated hydrocarbon in a 3:1 ratio at a controlled potential 1.8 V. The variation of electrochemical conditions of the experiment (solvent, reaction duration and the reagent/substrate ratio) affects the composition of the reaction products.

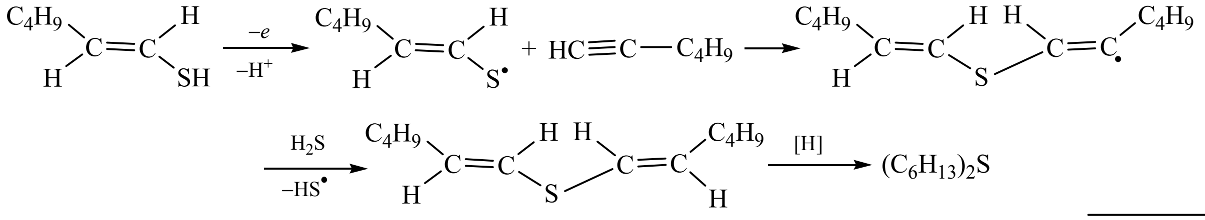
At the electrolysis of hydrogen sulfide with hex-1-yne in acetonitrile (MeCN), we fixed the accumulation of the adduct that oxidized at the anodic potential E_{pa} = 1.20 V. The sulfur-containing radical ($HS^{\bullet}$ or $PhS^{\bullet}$) are attached reversibly to the alkyne with the formation of β-alkylvinylthiyl radical in agreement with published data [2].



(1)

In the resulting mixture of *cis*- and *trans*-isomers the most stable *trans*-form of hex-1-en-1-thiol predominates. The subsequent electrochemical oxidation of this compound and saturation of the multiple bonds by the hydrogen released on the auxiliary electrode lead to the formation of the disulfide $(C_6H_{13}S)_2$ (5 wt % of the substrate) (E_{pa} = 1.6V) containing aliphatic substituents (Fig. 1).

Excess H_2S contributes to increasing the disulfide yield (6.3 wt % of the substrate), while increasing the concentration of hex-1-yne results in a predominant yield of aliphatic sulfide $(C_6H_{13})_2S$ (29.4 wt %, E_{pa} = 1.90 V), a product of the interaction of hexen-1-thiol with the starting substrate followed by hydrogenation:



(2)

The electrochemical properties of unsaturated hydrocarbons[a]

Compound	E_{pa}, V
Hex-1-yne	2.38
Hex-3-yne	2.14
Diphenylacetylene	1.98[b]
Buta-1,3-diene	2.03 [9]
2-Methylbuta-1,3-diene	2.03[b]
Cyclohexene	>2.00 [9]

[a] CH_3CN, carbon glass electrode, $c = 5\times10^{-3}$ M, Ag/AgCl/KCl, 0.1 M, n-Bu_4NBF_4. [b] Pt electrode, 0.1 M n-Bu_4NClO_4.

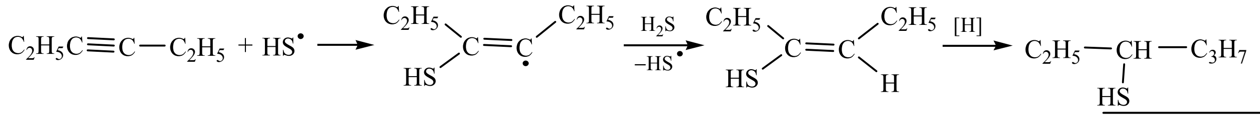
In the process of electrolysis an insoluble oligomeric product is formed containing, according to the data of IR spectroscopy, CH_2–CH_2 fragments, C=C (1666 cm^{-1}) and C–S (707 cm^{-1}) bonds, while the C=C–H stretching vibrations are not observed, indicating the cross-linking of the polymer chains through sulfide bridges.

At replacing MeCN by CH_2Cl_2, the same vinylthiol intermediate is initially fixed, and on increasing the electrolysis duration hexanethiol appears (29.4 wt % on the substrate, E_{pa} = 1.80 V, S–H 2573 cm^{-1}; C–S 640 cm^{-1}). In the background electrolyte after the reaction completion there are sulfur-containing polymer products (S–S 540 cm^{-1}). In dichloromethane, in contrast to the more polar acetonitrile, increasing the hex-1-yne concentration leads to a mixture of $C_6H_{13}SH$ and $(C_6H_{13}S)_2$ in 3:1 ratio.

In the case of hept-1-yne we obtained similar results. The reaction in CH_2Cl_2 medium at the oxidation potential of the reagent E_{pa} = 1.8 V initially leads to accumulation of a mixture of isomeric enethiols, which in the process of oxidation dimerize to form unsaturated disulfides followed by the saturation of the multiple bonds.

To determine the effect of the triple bond position on the reaction product composition, we performed the electrosyntheses using hex-3-yne and hydrogen sulfide under similar conditions. In CH_3CN the reaction product was thiol (E_{pa} = 1.65) (37.0 wt % on the substrate), which accumulated in the course of the reaction (Fig. 2).

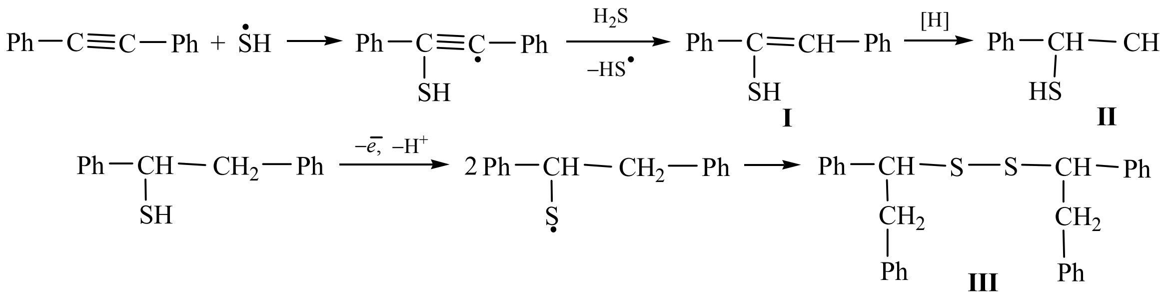
The presence of bulky ethyl substituents prevents dimerization of the formed $RS^•$ radicals [11], and the steric inaccessibility of the reactive center makes possible the reaction with hydrogen, which leads to the formation of *cis*-hex-3-ene-3-thiol, and then the corresponding aliphatic hexane-3-thiol.


(3)

The increase in hydrogen sulfide concentration has little effect on the yield of the main product. With increasing substrate concentration, a mixture of hexane-3-thiol and di(hexan-3-yl)sulfane in 1:4 ratio accumulates in the reaction mixture.

In dichloromethane, the main product is the polymer compound at any substrate/reagent ratio. The *cis*-vinylthiol was fixed in a negligible concentration.

Electrochemical initiation of the hydrogen sulfide reaction with diphenylacetylene showed that in acetonitrile a mixture of reaction products **I–III** is formed in a ratio of 1:2:1 with a predominance of thiol, as well as a small amount of polymeric products formed on the anode surface.



(4)

In the case of dichloromethane, only thiol **II** (yield 25.6% on consumed current) and disulfide (yield on current 1.6%) were produced (Fig. 3).

The reaction of hydrogen sulfide with buta-1,3-diene (CH_2Cl_2) resulted in the reaction product, which has a high anodic potential E_{pa} = 2.25 V (2 wt % to the substrate). The process of electrochemical oxidation of the compound is accompanied by the removal of a proton (E_{pc} = –0.10 V). This range of anode potentials is typical for the oxidation of alkenes [E_{pa} (oct-1-ene) = 2.23 V] [9]. Analysis of the infrared spectrum of the reaction product showed the presence of stretching vibrations of C=C (1640–1680 cm^{-1}) and C=C–H (3010 cm^{-1}) bonds. The ^1H NMR data indicate the formation of 2-methylhept-2-ene.

In the mixture of the electrolysis products was also found an insoluble polymeric product and C_2H_5SH (1 wt % on the substrate), E_{pa} = 1.78 V. The formation of the low molecular weight thiol may occur as a result of interaction of the thiyl radical with ethane, same as in the known method of producing hydrogen sulfide [12].

Reaction of isoprene with hydrogen sulfide in the electrochemical experiment leads to the formation of only the polymer product adsorbed on the surface of the working electrode. The polymerization reaction is initiated by the oxidized form of hydrogen sulfide: when the solution contains only the substrate the reaction at this potential does not occur. Adding of acid also does not cause adsorption of polymeric products on the electrode.

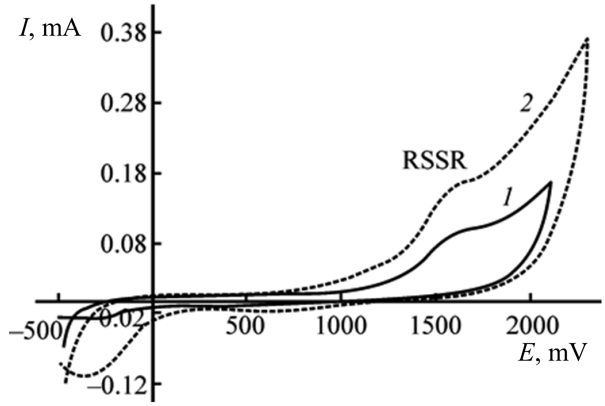


Fig. 1. Cyclic voltammograms of oxidation of the products of electrolysis of hex-1-yne with hydrogen sulfide 1:1 (MeCN, Pt-anode, Ag/AgCl/KCl, 0.1 M *n*-Bu_4NClO_4, sweep rate 0.2 V s^{-1}). (*1*) RSSR is dihexsylsulfide; (*2*) with added reference $(C_6H_{13}S)_2$. MeCN, Pt anode, Ag/AgCl/KCl. 0.1 M *n*-Bu_4NClO_4, 0.2 V s^{-1}.

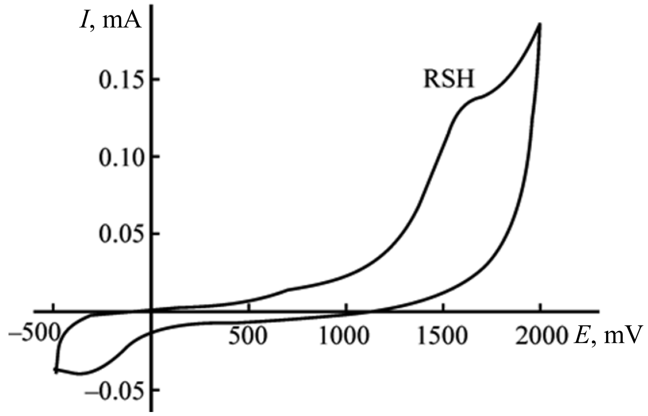


Fig. 2. Cyclic voltammograms of oxidation of the products of electrolysis of hex-3-yne with hydrogen sulfide (1:1). RSH is hexane-3-thiol (MeCN, Pt-anode, Ag/AgCl/KCl, 0.1 M *n*-Bu_4NClO_4, sweep rate 0.2 V s^{-1}).

Carrying out the reaction of the oxidized form of hydrogen sulfide with cyclohexene showed that at the anodic activation of the reagent cyclohexanethiol (2.9 wt % on the substrate, E_{pa} = 1.65 V), and disulfide (7.9 wt % on the substrate, E_{pa} = 1.25 V) were formed (Fig. 4), whose formation was confirmed by IR spectroscopy.

Thus, it is shown that the reaction of hydrocarbons of the series C_nH_{2n-2} with hydrogen sulfide under the conditions of anodic oxidation of the reagent proceeds in several ways: (1) addition of thiyl radicals ($HS^\bullet$, $RS^\bullet$) to multiple bonds to form thiols and sulfides, (2) dimerization of $RS^\bullet$ radicals leading to accumulation of disulfides, (3) saturation of multiple bonds, and (4) formation of polymeric compounds containing C–C, C=C, C–S, and S–S bonds.

Varying the reaction conditions (solvent and substrate nature, reaction duration, reagent ratio) allows performing the synthesis of various organic sulfur compounds. Hydrogen sulfide in the electrosynthesis acts as a bifunctional reagent, providing a source of the formation of new C–S bonds and the reactions of hydrogen redistribution.

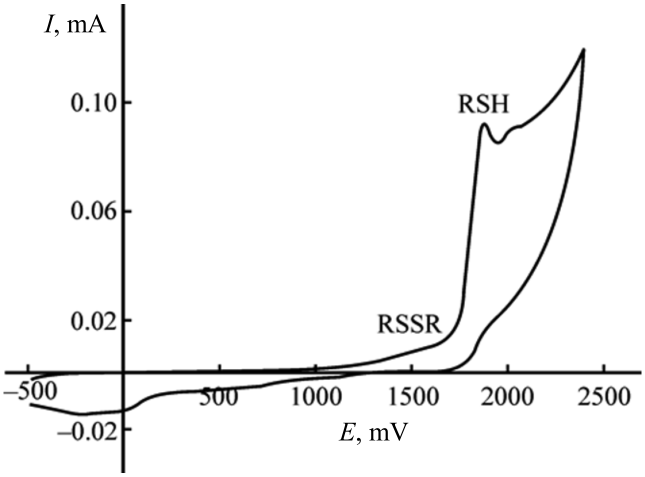


Fig. 3. Cyclic voltammograms of oxidation of the products of diphenylacetylene electrolysis with hydrogen sulfide. RSH is 1,2-diphenylethanetiol, RSSR is 1,2-bis(1,2-diphenylethyl)disulfane (CH_2Cl_2, Pt-anode, Ag/AgCl/KCl, 0.1 M *n*-Bu_4NClO_4, sweep rate 0.2 V s^{-1}).

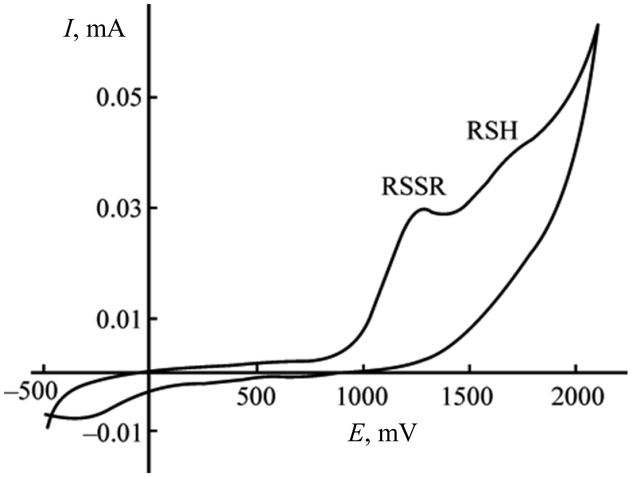


Fig. 4. Cyclic voltammograms of oxidation of the products of electrolysis of cyclohexene with hydrogen sulfide. RSH is cyclohexanethiol, RSSR is 1,2-dicycloheyldisulfane (CH_2Cl_2, Pt-anode, Ag/AgCl/KCl, 0.1 M *n*-Bu_4NClO_4, sweep rate 0.2 V s^{-1}).

EXPERIMENTAL

We used commercial unsaturated hydrocarbons: hex-1-yne (Aldrich, 97%), hex-3-yne (Aldrich, 99%), hept-1-yne (Aldrich, 98%), diphenylacetylene (Aldrich, 98 %), buta-1,3-diene (Aldrich, ≥ 99%), 2-methylbuta-1,3-diene (Aldrich, ≥ 99%), and cyclohexene (Merck, ≥ 99%).

As references were used hexanethiol (Aldrich, 99%), hexyl sulfide (Aldrich, 98%), dihexyl sulfide (Aldrich, 98%), cyclohexanethiol (Aldrich, 97%), ethanethiol (Aldrich, 97%).

The solvents acetonitrile (analytical grade) and dichloromethane (reagent grade) were purified by the methods described in [13, 14].

Background electrolyte (tetrabutylammonium perchlorate, n-Bu_4NClO_4, Fluka, > 99%) was subjected to double recrystallization from ethanol–water 1:1 mixture, the filtered off precipitate was dried at 50°C in a vacuum drying cabinet for 48 h.

To obtain hydrogen sulfide, in a round bottom flask of 250 ml were placed 70 g of crushed paraffin wax, 50 g of powdered sulfur, and 30 g of crushed calcined asbestos fiber [15]. The mixture was heated to 250–300°C. The liberated hydrogen sulfide was passed through water-free acetonitrile for 30 min to obtain a saturated solution. The concentration of hydrogen sulfide in solution was determined by potentiometric and gravimetric methods [16].

Electrochemical studies were carried out by the method of cyclic voltammetry (CVA) with a digital potentiostat IPC-Pro 8.60 [7]. To register the cyclic voltammograms a 2 ml three-electrode cell without a diaphragm was used. The working electrode was platinum electrode of 3.14 mm^2 surface area, or a carbon glass electrode of 2 mm^2 area. The reference electrode was saturated silver chloride electrode with water-impermeable diaphragm; auxiliary electrode was platinum of 70 mm^2 area. The rate of potential sweep was 0.2 V s^{-1}. The concentration of background electrolyte in the electrochemical cell solution was 0.10 M.

Microelectrolysis was performed with a potentiostat PI-50-1.1 using stationary platinum electrode of 30 mm^2 area and an Ag/AgCl/KCl electrode as a reference. In the three-electrode non-diaphragm cell of 2 ml volume containing background electrolyte solution in MeCN (CH_2Cl_2) was added substrate ($c = 5\times10^{-3}$ M) and hydrogen sulfide as a saturated solution in MeCN. The working electrode potential was set with a PR-8 programmer by 0.2–0.3 V more positive than the oxidation potential of the reagent (H_2S). The microelectrolysis duration was 3 h on an average [17].

The electrolysis products were isolated from the mixture by adding hexane (reagent grade). The precipitate formed in the background electrolyte was filtered off and washed with additional hexane. The resulting solution after filtration was distilled at the boiling point of hexane (68.7°C), the residue contained a mixture of the electrolysis products.

The IR spectra were recorded on a Fourier-transform infrared spectrometer SPM 1201 in the range of 400–5000 cm^{-1}, from the samples as tablets with KBr. The identification of products was done by comparison with the tables of frequencies of the IR spectra of organic compounds [18, 19].

The ^1H NMR spectra were recorded on a Bruker AVANCE DPX-200 spectrometer from solutions in $CDCl_3$, using tetramethylsilane as internal reference. For interpretation of the spectra we used the tables of ^1H NMR spectra of organic compounds [18–20].

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