# The radical cation of hydrogen sulfide and related organic reactions*

*N. T. Berberova* and E. V. Shinkar'*

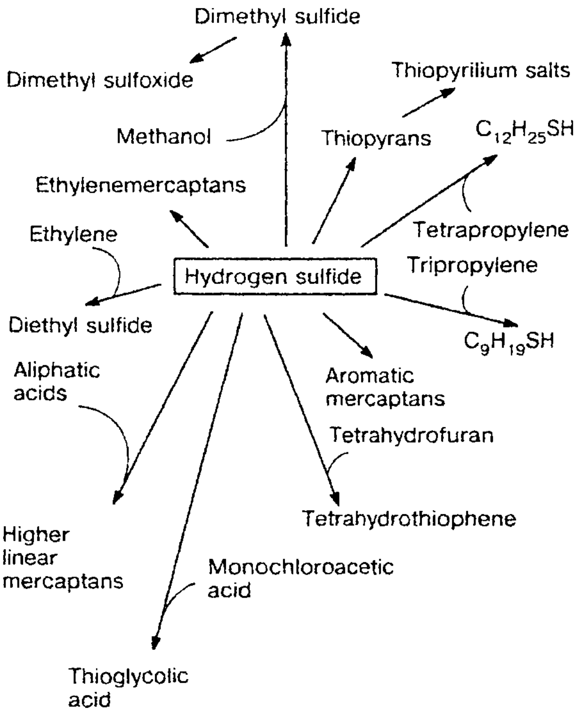
*Astrakhan State Technical University,*
*16 ul. Tatishcheva, 414025 Astrakhan, Russian Federation.*
*Fax: +7 (812 2) 25 6427. E-mail: astu@astu.astranet.astu*

The electrochemical and chemical oxidation (by hindered *o*-benzoquinones or $NOClO_4$) of $H_2S$ in nonaqueous solutions (MeCN) proceeds with the donation of one electron. The formation of the unstable radical cation of hydrogen sulfide was detected by cyclic voltammetry. The radical cation decomposes to form $H^+$ and the $HS^{\cdot}$ radical. The generation of the hydrogen sulfide radical cation was confirmed by ESR spectroscopy in a frozen Freon matrix. The possibility of using the hydrogen sulfide radical cation in the synthesis of organosulfur compounds under mild conditions was studied.

**Key words:** radical cation of hydrogen sulfide, oxidative activation, cyclic voltammetry, ESR spectroscopy, reaction mechanism.

All hydrogen sulfide in natural gas is usually burned for the preparation of elemental sulfur.[1,2] The possibilities of using hydrogen sulfide[3] are wider than this process alone. Hydrogen sulfide, as Scheme 1 demonstrates, is a valuable raw material for syntheses of various organosulfur compounds.

**Scheme 1**



The variety of products of organic synthesis involving $H_2S$ and wide use of them in various areas of chemical industry emphasize the urgency of studying the mechanism of reactions in which hydrogen sulfide acts as the main reactant. These reactions are usually difficult to perform because of the low reactivity of molecular hydrogen sulfide. As a rule, all of them proceed at elevated temperature and pressure or under UV irradiation. In this work, we consider a new method for the preparation of organosulfur compounds from hydrogen sulfide under relatively mild conditions with the electrochemical and chemical activation of this reagent.

## Results and Discussion

According to the data of cyclic voltammetry (CV), in nonaqueous media (MeCN) hydrogen sulfide is electrochemically oxidized in the one-electron irreversible step at a potential of 1.6 V. The secondary wave exhibits the peak of proton reduction ($E_{pc}$ = −0.2 V) identified by the addition of anhydrous perchloric acid (Fig. 1, *a*). Microelectrolysis of hydrogen sulfide at 1.8 V results in the appearance of an anodic peak at zero potential. This peak corresponding to the formation of hydrogen polysulfides (Fig. 1, *b*) was identified by the addition of a freshly prepared solution of polysulfans. Opalescence of the solution due to the precipitation of elemental sulfur was observed during microelectrolysis.

Diffusion is the limiting step of hydrogen sulfide oxidation in nonaqueous media because the maximum current as a function of the square root of the potential sweep rate ($\upsilon$ = 0.5—100 V $s^{-1}$) and the calibrating plot are linear and pass through the origin.[4] The data presented above suggest that the electrochemical oxidation

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* The concept of the work was proposed by Prof. O. Yu. Okhlobystin. The first electrochemical experiments were performed when he was alive.

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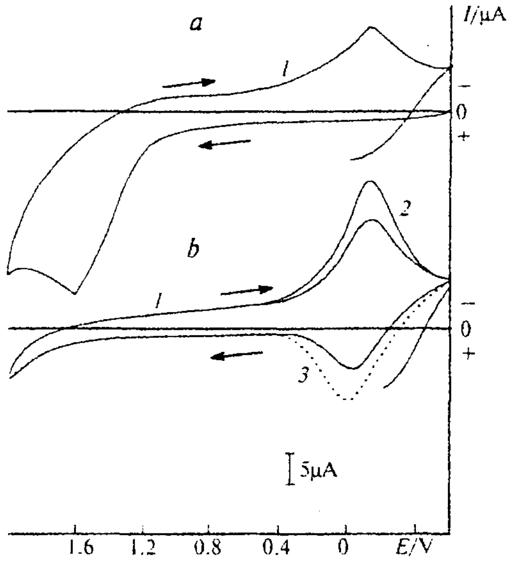


**Fig. 1.** Cyclic voltammograms of hydrogen oxidation before (*a*) and after electrolysis (*b*) without additives (*1*) and in the presence of additives of $HClO_4$ (*2*) and polysulfans (*3*).

of hydrogen sulfide in anhydrous MeCN proceeds *via* Scheme 2.

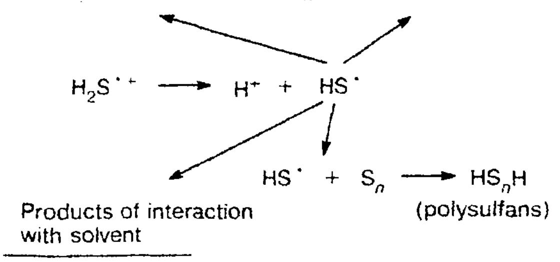
**Scheme 2**

$$H_2S \xrightarrow{-e} H_2S^{\cdot +}$$

The radical cation of hydrogen sulfide was detected by ESR in the frozen matrix.* Under γ-irradiation (77 K) of Freon-113 ($CF_2ClCFCl_2$) containing 0.5% hydrogen sulfide, we detected a triplet ($a_{2H}$ = 29 G) attributed to the hydrogen sulfide radical cation, and its lifetime under these conditions is 15 min (Fig. 2).

The radical cation that formed is unstable under standard conditions and decomposes with the elimination of a proton, which is thermodynamically most favorable.[5] The reactions accompanying the fragmentation of the hydrogen sulfide radical cation in nonaqueous media can be presented by Scheme 3.

**Scheme 3**



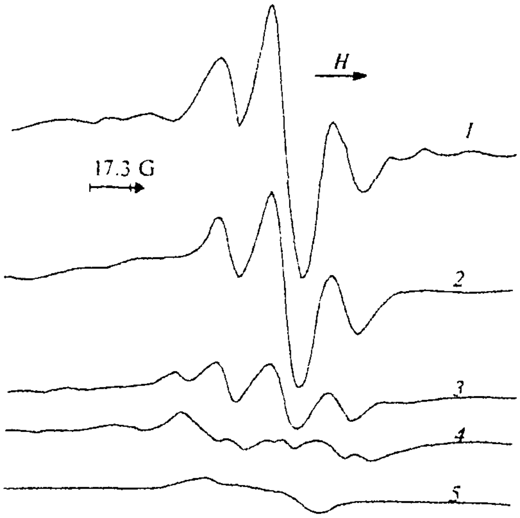


**Fig. 2.** ESR spectrum of the hydrogen sulfide radical cation (Freon-113, 0.5% $H_2S$, 77 K, γ-irradiation). Spectra *1—5* were obtained at intervals of 3 min.

Hydrogen sulfide dissolved in water is a weak acid with $pK_a$ = 7.04. At the same time, hydrogen sulfide oxidation to the radical cation sharply increases the acidic properties of hydrogen sulfide. For the experimental estimation of $pK_a$ of the oxidized form of hydrogen sulfide, we used the Bordwell method[6] based on the combination of $pK_{RH}$ and the oxidation potentials of the acid ($E^{ox}_{RH}$) and conjugated base ($E^{ox}_{R^-}$):

$$pK_{RH^{\cdot +}} = pK_{RH} + (E^{ox}_{R^-} - E^{ox}_{RH}) \cdot 23.06/1.37.$$

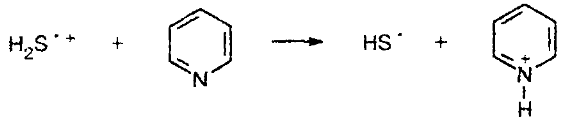
The insertion of the oxidation potentials of hydrosulfuric acid and conjugated base $HS^-$ obtained in the electrochemical experiment and measured immediately after the end of electrolysis of $H_2S$ made it possible to calculate the acidity of the hydrogen sulfide radical cation:

$$pK_{H_2S^{\cdot +}} = 7.04 + (-0.2 - 1.6) \cdot 23.06/1.37 \approx -23.$$

This value indicates the high acidic properties of the radical cation because it is measurable with $pK_a$ of superacids (for example, for $SbF_5$—$FSO_3H$, $pK_a < -20$).[7]

The electrochemical experiment showed that Lewis organic bases, which do not enter into the reaction with molecular hydrogen sulfide (Fig. 3, *a*) in MeCN are almost immediately protonated by the superacidic radical cation $H_2S^{\cdot +}$ (Scheme 4).

**Scheme 4**



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* The work was performed in cooperation with Doctor of Science V. N. Belevskii (M. V. Lomonosov Moscow State University).

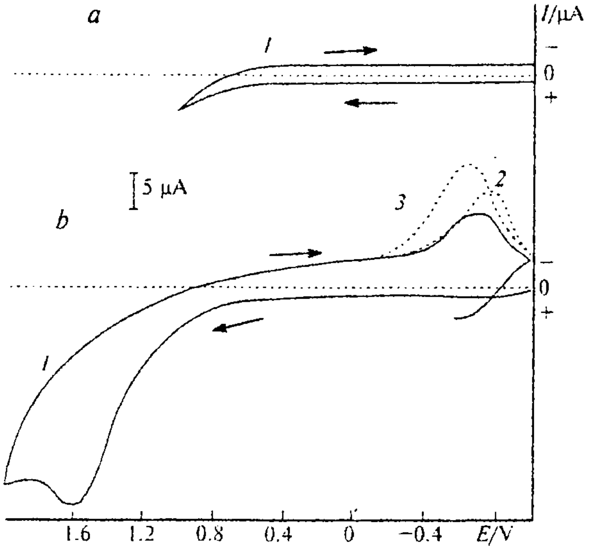


**Fig. 3.** Cyclic voltammograms of hydrogen sulfide in the presence of pyridine (*1*), quinoline (*2*), and acridine (*3*) before the generation of the radical cation $H_2S^{\cdot +}$ (*a*) and after the electrochemical oxidation of $H_2S$ (*b*) (concentrations of $H_2S$ and substrates were $5 \cdot 10^{-3}$ mol $L^{-1}$ each).

The reduction peaks of cations with reduction potentials of −0.68, −0.74, and −0.62 V (Fig. 3, *b*) were detected in CV due to the reaction of electrochemically oxidized hydrogen sulfide with weak organic bases (pyridine, quinoline, and acridine, respectively).

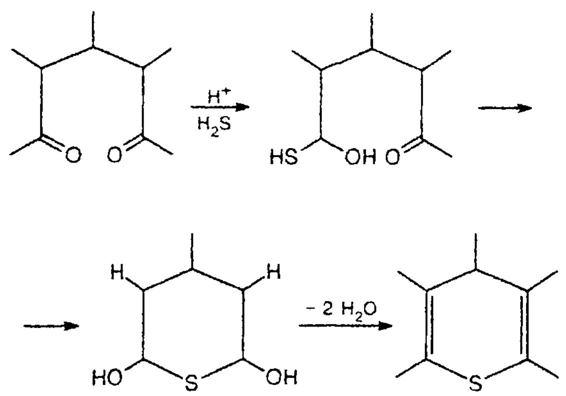
The hydrogen sulfide radical cation can be generated chemically in nonaqueous media by one-electron oxidants. The use of nitrosonium perchlorate as an oxidant confirmed the ability of the hydrogen sulfide radical cation to manifest the properties of a strong acid in reactions with weak organic bases.

The oxidation of hydrogen sulfide in nonaqueous media to the radical cation sharply enhances its acidic function and imparts to it the dual reactivity of a radical and an electrophile. Under electrochemical oxidation conditions, the hydrogen sulfide radical cation is capable of entering into electrophilic addition to substrates with a multiple bond and reacting with aromatic hydrocarbons to form mercaptans. Several examples of similar type are presented in the work.

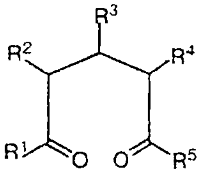
**Oxidative activation of hydrogen sulfide in cyclization with substituted 1,5-diketones.** The products of the reaction of substituted 1,5-diketones with hydrogen sulfide (thiopyrans and their oxidized forms, thiopyrilium salts) are of interest due to possibilities of use in various areas: biochemistry, medicine, photochemistry, and the chemistry of dyes.[8]

Synthesis of substituted thiopyrans is usually performed in the presence of strong acids. It is considered[9] that intermediate hemithioacetals are cyclized at the sulfur atom (Scheme 5).

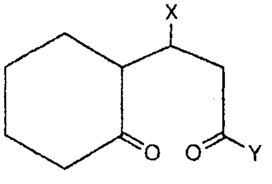
**Scheme 5**



Taking into account the strong acidic properties of the hydrogen sulfide radical cation, we proposed a preparatively simple method for the synthesis of thio derivatives from substituted 1,5-diketones and hydrogen sulfide under the conditions of generation of the hydrogen sulfide radical cation by the electrochemical method. We used 1,5-diketones **1a—g**, **2a,b**,* with which hydrogen sulfide does not react, under standard conditions, without addition of strong acids.



**1a—h**



**2a,b**

| **1** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|
| **a** | Ph | H | H | H | Ph |
| **b** | Ph | H | $p$-$ClC_6H_4$ | H | Ph |
| **c** | $p$-$MeOC_6H_4$ | H | H | H | $p$-$MeOC_6H_4$ |
| **d** | Ph | H | Ph | Me | Ph |
| **e** | $p$-$MeOC_6H_4$ | H | $p$-$MeOC_6H_4$ | H | $p$-$MeOC_6H_4$ |
| **f** | $p$-$ClC_6H_4$ | H | Me | H | $p$-$ClC_6H_4$ |
| **g** | Ph | H | Ph | H | Ph |
| **h** | 2,4-$(MeO)_2C_6H_3$ | H | Ph | H | 2.4-$(MeO)_2C_6H_3$ |

**2:** X = $p$-$MeOC_6H_4$, Y = Ph (**a**); X = Y = Ph (**b**)

The oxidation potentials of 1,5-diketones in MeCN lie in the region from 2.0 to 2.4 V (depending on the nature of the substituents), *i.e.*, in the region of values more positive than the oxidation potential of hydrogen sulfide. During the electrochemical initiation of the reaction, the reactants did not interact if the potential sweep width did not cover the region of generation of the hydrogen sulfide radical cation (1.6 V). When the

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* The 1,5-diketones[9] were a generous gift from the Laboratory of Synthesis of Heterocyclic Compounds (N. G. Chernyshevskii Saratov State University).

**Table 1.** Oxidation ($E_{pa}$) and reduction potentials ($-E_{pc}$) of the preparative electrolysis products of 1,5-diketones in the presence of $H_2S$

| Diketone | $E_{pa}$ | $-E_{pc}$ | Diketone | $E_{pa}$ | $-E_{pc}$ |
|---|---|---|---|---|---|
| | V | | | V | |
| **1a** | 1.50 | 0.50 | **1f** | 1.68 | 0.28 |
| **1b** | 1.60 | 0.30 | **1g** | 1.65 | 0.25 |
| **1c** | 1.70 | 0.40 | **1h** | 1.80 | 0.28 |
| **1d** | 1.65 | 0.55 | **2a** | 1.67 | 0.37 |
| **1e** | 1.75 | 0.38 | **2b** | 1.60 | 0.48 |

sweep width increased to 1.8 V, the inverse scan of the voltammogram exhibited two peaks in the anodic region ($E_{pa}' = 1.1$ V and $E_{pa} = 1.50$—1.8 V, depending on the structure of the initial diketone) and one peak in the cathodic region ($E_{pc} = -0.28$—$-0.55$ V). The anodic peaks were assigned to the formation of hemithioacetals and thiopyrans, whereas the cathodic peaks were attributed to thiopyrilium cations, which was confirmed by the addition of authentic samples.

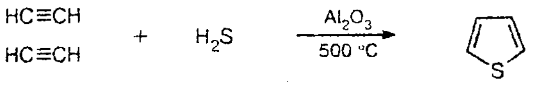
After electrolysis at the oxidation potential of hydrogen sulfide (Table 1), we observed the waves of thiopyrans and their dehydrated forms. The mechanism of formation of sulfur-containing heterocycles is identical to the classical scheme presented above. The distinction is that the hydrogen sulfide radical cation is the proton donor necessary for an increase in the reactivity of diketone rather than additives of acids.

The electrochemical model of cyclization of 1,5-diketones with the activated form of hydrogen sulfide was confirmed by preparative experiments in which the anodic function was replaced by the effect of a one-electron oxidant, hindered 3,5-di-*tert*-butyl-*o*-benzoquinone. It was shown by CV monitoring that the starting 1,5-diketones did not react with this quinone. However, when hydrogen sulfide was passed through the system (quinone—diketone), peaks indicating the formation of thiopyrans and thiopyrilium salts appeared in CV.

It follows from the aforesaid that the oxidative activation of $H_2S$ (by the electrochemical and chemical methods) can be used for the synthesis of heterocycles from hydrogen sulfide and 1,5-diketones. Thus, the hypothesis that the high reactivity of the hydrogen sulfide radical cation makes it possible to avoid the traditional use of strong acids for the preparation of thiopyrans and thiopyrilium salts was experimentally substantiated.

**Oxidative activation of hydrogen sulfide in the synthesis of thiophene.** An industrial method of synthesis of thiophene is the Chichibabin reaction of acetylene with hydrogen sulfide at 500—600 °C on alumoxide catalysts with various supported promoting additives (chrome, nickel, or cobalt oxides)[10] (Scheme 6).

Scheme 6



The high temperature is necessary for the homolysis of the S—H bond, *i.e.*, the reaction occurs *via* the radical mechanism. It is reasonable to assume that the activation barrier can be decreased if the reaction is performed by a different, radical-ion route.

With this purpose we used electrochemical and chemical hydrogen sulfide activation in nonaqueous media. It has been preliminarily found that acetylene does not react with hydrogen sulfide at room temperature without a catalyst. The potentials of oxidation in MeCN and ionization of acetylene and hydrogen sulfide are 2.1, 1.6 V and 11.4, 10.5 eV, respectively. Therefore, the more easily activated hydrogen sulfide is the main reactant.

After exhaustive electrolysis at $E = 1.8$ V in the presence of acetylene, we detected the wave of thiophene oxidation on the cyclic voltammogram (Fig. 4). The final product was identified by the addition of the chemically pure sample. The formation of thiophene in the solution under study was also confirmed by GLC and the qualitative indophenine reaction.[11]

The experimental electrochemical data agree with the experiments in which the hydrogen sulfide radical cation was generated by one-electron oxidants: 3,5-di-*tert*-butyl-*o*-benzoquinone or nitrosonium perchlorate. In all experiments, we observed the formation of thiophene, but its yield was negligible when the reaction was performed in a solution.

To increase the yield, we attempted to prepare thiophene under the heterogeneous catalysis conditions in a model quartz reactor with a supported catalyst.

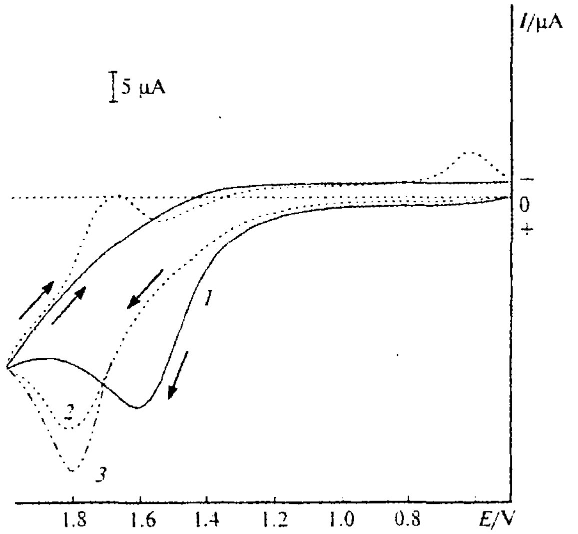
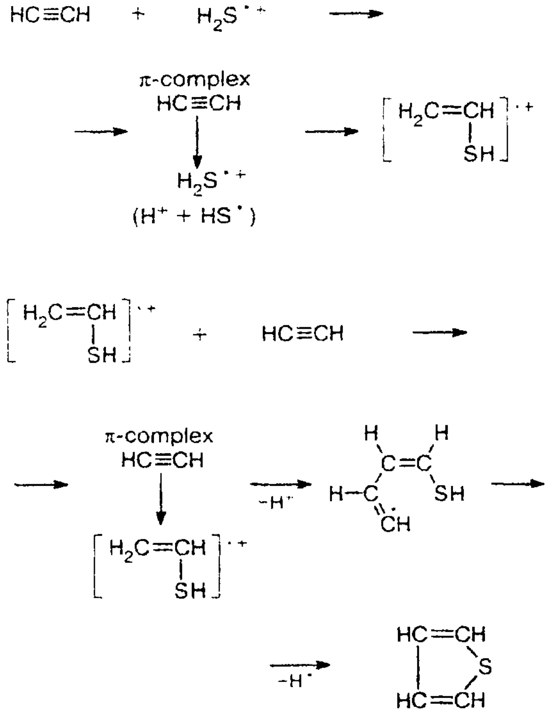


**Fig. 4.** Cyclic voltammograms of a mixture of acetylene with hydrogen sulfide before electrolysis (*1*), after electrolysis (*2*), and after the addition of the standard, thiophene (*3*).

Alumosilicates pre-impregnated with a 10% solution of 3,5-di-*tert*-butyl-*o*-benzoquinone in MeCN were used as the latter. This increased the number of active sites of the catalyst and simultaneously provided its multiple and independent regeneration because the oxidation of hydrogen sulfide by quinone is cyclic. The yield of thiophene per turnover was ~15%.

The synthesis of thiophene under the conditions of hydrogen sulfide oxidative activation on the electrode and catalyst surface demonstrates the existence of the radical-ion reaction route that can be presented by Scheme 7.

**Scheme 7**

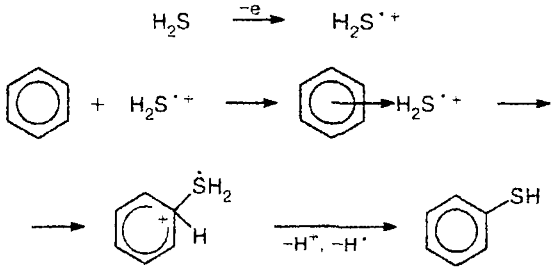


**Reaction of radical cation of hydrogen sulfide with aromatic hydrocarbons.** Synthesis of aromatic mercaptans is a labor-consuming process that requires harsh conditions (UV irradiation, high temperature and pressure).[12] Under these conditions, the formation of thiophenols occurs *via* the radical mechanism through the step of pre-generation of the thiyl radical.

The synthesis of aromatic mercaptans involving hydrogen sulfide, under milder conditions, requires the activation of either an aromatic substrate or the attacking reactant, $H_2S$. The following hydrocarbons were chosen as the starting substrates: benzene, toluene, naphthalene, and anthracene, whose oxidation potentials in acetonitrile on the Pt anode are 2.63, 2.1, 1.77, and 1.4 V, respectively (relative to Ag/AgCl). The special control experiments confirmed that the substrates used do not react with hydrogen sulfide under standard conditions for a long time.

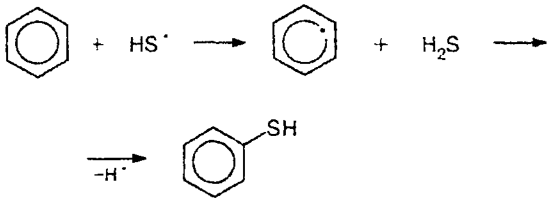
By contrast, the exhaustive electrolysis of benzene and hydrogen sulfide at $E_{pa}$ = 1.8 V results in a change in the color of the solution and formation of the reaction product. The cyclic voltammogram (after the traces of hydrogen sulfide were removed) exhibited two oxidation peaks at $E_{ps}'$ = 0.8 V and $E_{ps}''$ = 1.4 V corresponding to the oxidation of the standard, thiophenol.

**Scheme 8**



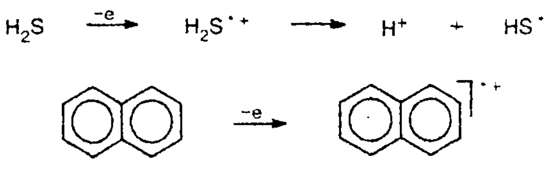
The addition of the standard (thiophenol) to the electrolysis products resulted in an increase in the intensity of the peaks (Fig. 5). In addition, the synthesis of thiophenol during electrolysis of a hydrogen sulfide—benzene mixture was confirmed by GLC and IR spectroscopy. After the generation of the hydrogen sulfide radical cation, the reaction with benzene proceeds *via* the classical scheme (see Scheme 8), while the radical route also cannot be ruled out, *i.e.*, the participation of the thiyl radical formed due to the fragmentation of $H_2S^{\cdot +}$ (Scheme 9).

**Scheme 9**

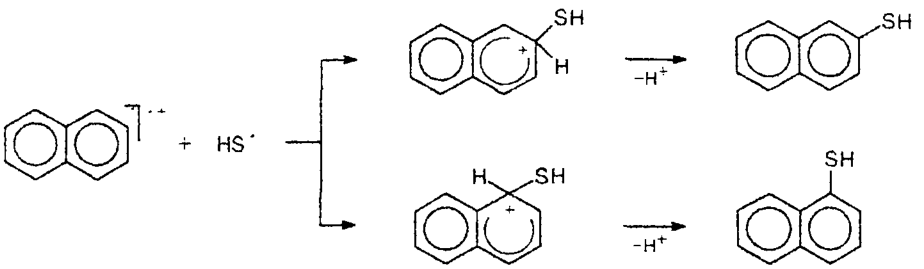


In the case of the preparative electrolysis of hydrogen sulfide with naphthalene and anthracene, the mechanism of electrochemical synthesis of thiophenols somewhat differs because at the anodic potential $E_{pa}$ = 1.8 V both the substrates (aromatic hydrocarbons) and reactant can be oxidized to the corresponding radical cations (Scheme 10).

**Scheme 10**



**Scheme 11**



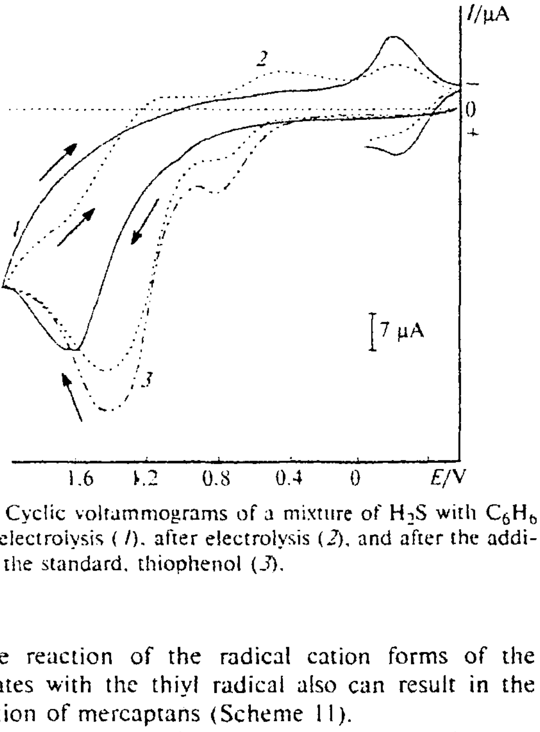


**Fig. 5.** Cyclic voltammograms of a mixture of $H_2S$ with $C_6H_6$ before electrolysis (*1*), after electrolysis (*2*), and after the addition of the standard, thiophenol (*3*).

The reaction of the radical cation forms of the substrates with the thiyl radical also can result in the formation of mercaptans (Scheme 11).

Thus, the electrochemical and, perhaps, chemical oxidative initiation of hydrogen sulfide can be used for the synthesis of aromatic mercaptans under rather mild conditions.

## Experimental

Cyclic voltammograms were recorded on an automated system for electrochemical measurements consisting of a PI-50.1 potentiostat, a PR-8 programmer, a three-electrode diaphragm-free cell, and an IBM 486 DX 100 personal computer. The latter was used for monitoring and processing of experimental data.

A stationary needle-like platinum electrode ($S$ = 3.14 mm$^2$) was used as the working electrode. The reference electrode was a saturated silver chloride electrode with a waterproof diaphragm. A Pt plate ($S$ = 70 mm$^2$) served as the auxiliary electrode. Acetonitrile was used as the working solvent.[13] $Bu_4NClO_4$ (0.1 mol L$^{-1}$) was used as the supporting electrolyte.[14] The potential sweep rate was 0.5 V s$^{-1}$.

Exhaustive electrolysis was carried out in MeCN ($Bu_4NClO_4$ (0.1 mol L$^{-1}$) was the supporting electrolyte) using Pt electrodes ($S$ = 70 mm$^2$) at the potential $E_{pa}$ = 1.8 V in a diaphragm-free cell. The time of electrolysis was 2 h. The initial concentration of the substrates was 5 · 10$^{-3}$ mol L$^{-1}$. The constant rate of hydrogen sulfide supply to an electrochemical cell was 2.0—3.0 L h$^{-1}$. Hydrogen sulfide was prepared by the previously described procedure.[15a] The concentration of hydrogen sulfide was determined gravimetrically and potentiometrically.[16] The number of electrons participating in redox processes was calculated by comparison with the standard, ferrocene (Fluka).

The spectrum of the hydrogen sulfide radical cation was recorded in a frozen Freon-113 matrix that undergoes phase transition at 110 K under γ-irradiation. Commercially available hydrogen sulfide (Riken Keiki Co., Ltd. Japan) was used for recording of the spectra.

Polysulfans were prepared by the previously described procedure.[15b] Nitrosonium perchlorate used as the one-electron oxidant was synthesized by the known procedure.[15c] The hydroxy form that formed due to electrolysis of diketone and hydrogen sulfide was identified by comparison with published data on the oxidation potentials of hydroxy compounds.[17] For the identification of the thiopyrilium cation, thiopyrilium salts were prepared by the previously described procedure.[18]

Electrochemically synthesized organosulfur compounds (thiophene, thiophenol) were analyzed on an IKS-29 spectrometer in Nujol in the 400—4200 cm$^{-1}$ interval. Chromatographic analysis was carried out on a Tsvet-500 gas chromatograph with a flame-ionization detector (the temperature of the column was 190 °C, and the temperature of the evaporator was 200 °C). A 2-m column with a stationary polar phase Carbowax-20M on Chromaton N-AW-CMDS was used. Thiophene and thiophenol in ampules ("for chromatography") were used for the identification of electrolysis products and for chromatographic analysis.

Elemental sulfur obtained electrochemically in the exhaustive electrolysis of hydrogen sulfide was identified by X-ray fluorescence analysis on a VRA-30 scanning spectrometer.

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