

Electrochemical Synthesis of Aromatic Sulfur Compounds in Ionic Liquids

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Abstract—Electrochemical properties of ionic liquids (pyridinium and imidazolium salts) and the effect of additives of organic solvents on the electrochemical determination of organic compounds in ionic liquids have been studied. Transformations of aromatic and aliphatic sulfur compounds in ionic liquids in the presence of aromatic substrates are discussed. A new method has been proposed for identification of organic sulfur compounds – gas chromatography on columns with ionic liquid as the active phase.

Keywords: ionic liquid, aromatic sulfur compound, electrochemical synthesis, extraction

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Nowadays, the interest to ionic liquids has rapidly emerged. Ionic liquids have been recognized for a number of attractive advantages: they are practically non-volatile, non-flammable, readily dissolve many inorganic, organic, and organometallic compounds (involving gases), they have been used as efficient extracting agent that can be easily regenerated and reused [1]. The ionic liquids with imidazolium $[R^1R^2Im]^+$ and pyridinium $[R^1R^2Py]^+$ cations are widely used. Most of them are highly stable and possess lyophilic properties over a wide range of temperatures. The possibility to vary cations and anions allows designing of ionic liquids for specific tasks. Methyl and *n*-butyl groups are most often used as the hydrocarbon substituents R^1 and R^2 . The anionic part can contain different anions: Cl^- , Br^- , I^- , PF_6^- , BF_4^- , etc.

The use of ecologically friendly reagents is one of the basic principles of “green” chemistry [2]. The electrochemical synthesis is practically impossible in the absence of solvent; ionic liquids can be used as the alternative reaction medium, since they are electric conductors. Being electrochemically stable, they allow performing of electrochemical experiments over a wide range of potentials. Physico-chemical properties of ionic liquids and the nature of the used electrodes are important points to be considered in electrochemical

studies. Investigation of the process of electrochemical decomposition of $[1-Bu-3-MeR^1Im]^+X^-$ ($X = PF_6, BF_4$) has shown that these ionic liquids are not always inert at a carbon glass electrode, but the use of tungsten electrode improves their stability [3].

The topicality of the search for novel methods of synthesis of aromatic sulfur compounds (thiophenols, thiocresols, aromatic sulfides, disulfides, etc.) is mainly due to their valuable properties. These compounds, possess antioxidant properties; on top of that, they are precursors in the synthesis of organometallic compounds exhibiting proliferative properties [4]. Aromatic sulfur compounds have been used for metal protection against corrosion, as antimicrobial drugs, photosensibilizers in color and IR photography, accelerators of vulcanization, and inhibitors of rubber aging [5, 6]. Among the studies on transformations of sulfur compounds in the pyridinium and imidazolium ionic liquids medium, the report [7] on transformation of benzylthiol catalyzed by cobalt phthalocyanine in the medium of imidazolium ionic liquid, leading to the corresponding disulfide in 95% yield, is remarkable.

In this work we studied the transformations of aliphatic and aromatic sulfur compounds in the medium of ionic liquids in order to prepare sulfur compounds valuable for medicine.

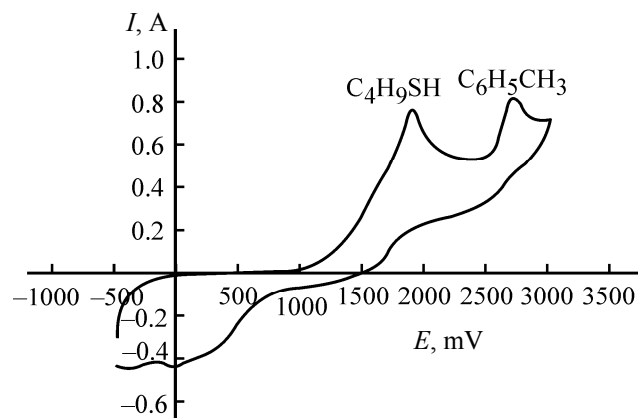


Fig. 1. Cyclic voltamperogram for electrochemical oxidation of C_4H_9SH and $C_6H_5CH_3$ in $[1-Bu-3-MeIm]PF_6$ ($\nu = 200$ mV/s, $Ag/AgCl$, $c = 5 \times 10^{-3}$ mol/L, Pt electrode).

In order to optimize the conditions of the electrochemical transformations of sulfur compounds in ionic liquids, we determined the electrochemical “window” of ionic liquids stability, elucidated the effect of the solvent on the viscosity and electrochemical sensitivity, and found the optimal ionic liquid–organic solvent ratio, temperature, and the material of working electrode.

N-Butylpyridinium and 1-butyl-4-methylpyridinium tetrafluoroborates {[1-BuPy]BF₄ (**1**) and [1-Bu-4-MePy]BF₄ (**2**)} as well as salts of 1-butyl-3-methylimidazolium with BF₄⁻ (**3**), PF₆⁻ (**4**), and Br⁻ (**5**) anions were used as ionic liquids. $C_6H_5CH_2SH$ and *n*- C_4H_9SH were selected as the model sulfur compounds.

The values of the electrochemical “window” (ΔE) for the studied ionic liquids characterizing the difference between the anodic and cathodic potentials for the redox processes are given in the table. As followed from the obtained results, all the studied ionic liquids except for [1-Bu-3-MeIm]Br exhibited a wide electrochemical stability range ΔE of 5–6 V. Electroconducting properties of ionic liquids and the high

Values of electrochemical “window” for ionic liquids **1–5**

Ionic liquid	E_{ox}^{max} , V	E_{red}^{max} , V	ΔE , V
[1-BuPy]BF ₄ (1)	3.5	-1.6	5.1
[1-Bu-4-MePy]BF ₄ (2)	3.7	-1.7	5.4
[1-Bu-3-MeIm]BF ₄ (3)	3.0	-3.0	6.0
[1-Bu-3-MeIm]PF ₆ (4)	3.4	-3.5	6.7
[1-Bu-3-MeIm]Br (5)	1.0	-1.2	2.2

value of ΔE allow to register the redox stages for thiols [$E_{ap}(C_4H_9SH) = 1.8$ V] as well as for hardly oxidizable substrates [$E_{ap}(C_6H_5CH_3) = 2.75$ V] in the absence of background electrolyte at room temperature (Fig. 1). A weak peak at 1.55 V was also present on the voltamperogram, corresponding to the product of C_4H_9SH dimerization ($C_4H_9SSC_4H_9$), pointing at the pathway of sulfur compounds transformations in the ionic liquid [8].

Electrochemical studies with using the [1-Bu-3-MeIm]Br salt were performed at 80°C, since at room temperature the salt was crystalline. The low ΔE value for [1-Bu-3-MeIm]Br did not allow for the electrochemical oxidation at potentials higher than 1.0 V (oxidation of bromide ion). The use of [1-Bu-3-MeIm]Br was possible only for easily oxidizable sulfur compounds, like polysulfanes.

One of drawbacks of ionic liquids is their high viscosity slowing down the transport of the reagents to the substrates. The issue can be resolved by addition of small amount of an aprotic solvent.

According to modern studies [9], ionic liquids based on imidazolium salts exist in the form of supramolecular polymeric structures with high degree of self-organization. Mixing of ionic liquids with different solvents affords the nanostructured materials containing both polar and nonpolar domains [10]. Addition of organic solvent to an ionic liquid leads to solvation of its cations and anions that results in enhanced dissociation of the liquid, decrease of its viscosity, and increase of the conductivity. Even though addition of a co-solvent slightly reduces the range of the electrochemical “window” of the ionic liquid, the decrease of its viscosity improves the conditions of electrolysis and facilitates the transport of the charged species in the electroconductive medium.

In the present work, acetonitrile was used as the aprotic solvent for viscosity modification. In order to optimize the solvent–ionic liquid ratio, electrochemical experiments using ferrocene as reference were performed.

To increase the solubility of ferrocene in [Bu-3-MeIm]BF₄, the mixture was pre-heated to 80°C, and then cooled to ambient. Addition of acetonitrile led to the increase of electrochemical sensitivity of the medium, making it less viscous and affecting the value of the ferrocene oxidation current (Fig. 2). The highest current of ferrocene oxidation was observed at the ionic liquid–organic solvent ratio to 1 : 1.

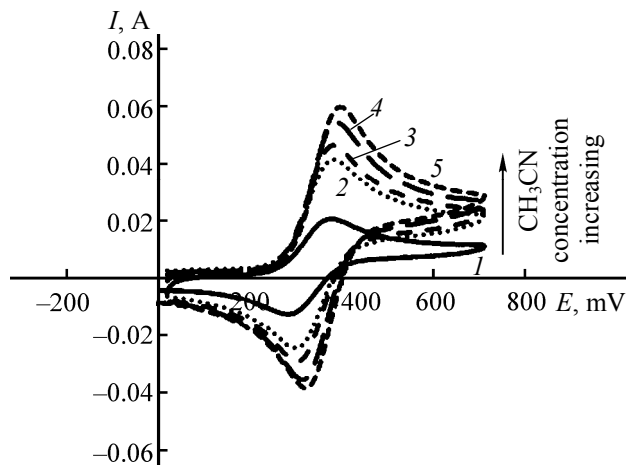


Fig. 2. Cyclic voltamperogram for ferrocene oxidation on Pt electrode at room temperature in a [Bu-3-MeIm]BF₄-CH₃CN mixture ($v = 200$ mV/s, Ag/AgCl, Pt electrode) at [Bu-3-MeIm]BF₄-CH₃CN ratio: (1) 5 : 1, (2) 1.4 : 1, (3) 1.25 : 1, (4) 1.1 : 1, and (5) 1 : 1.

Comparison of electrochemical properties of ferrocene at different electrodes nature showed that the highest current value was reached when using platinum electrode. In the case of carbon glass electrode, the value of the ferrocene oxidation current was almost twice lower (Fig. 3).

Hence, the optimal conditions for carrying out the experiments on electrochemical transformations of sulfur compounds in ionic liquids were found.

Further on, those conditions were used to study the transformations of benzylthiol C₆H₅CH₂SH and butanethiol C₄H₉SH in the presence of toluene. The electrolysis of C₆H₅CH₂SH at the potential of 2.0 V in the 1-BuPy][BF₄-CH₃CN 1 : 1 mixture on Pt electrode at room temperature resulted in the formation of the sulfide, dibenzyl and nanosized sulfur, on top of the disulfide ($E_{ap} = 1.65$ V) (Scheme 1).

The major product of the electrolysis was the disulfide formed in 95% yield. In the presence of air oxygen, the formed disulfides were further oxidized into the corresponding thiosulfonates, which are biologically active compounds promising for preparation of drugs exhibiting anti-neurotic, anti-asthmatic, and anti-allergenic activity [11] (Scheme 2).

We have earlier shown that single-electron oxidation of thiols in organic aprotic solvents leads to formation of cation-radical species, being deprotonated to formation the radicals [12].

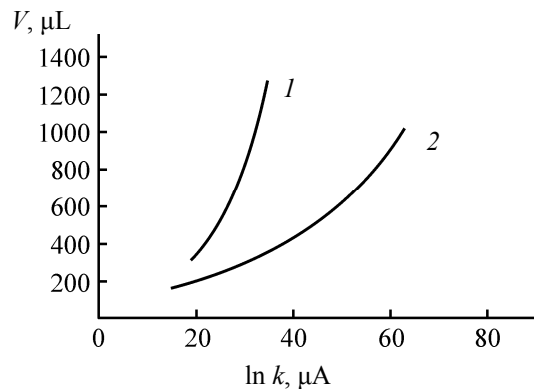
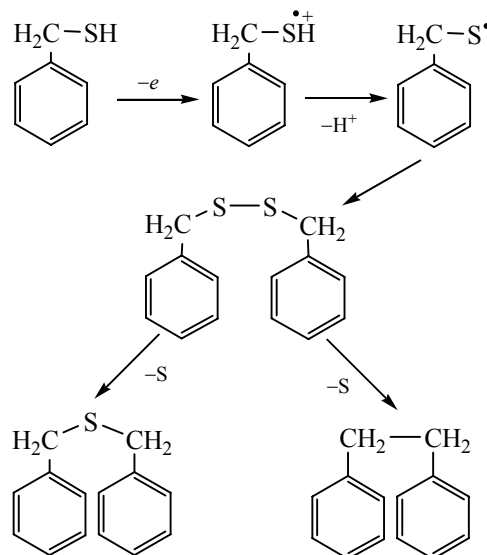


Fig. 3. Exponential dependence of the ferrocene oxidation current value on the content of acetonitrile in the ionic liquid. Volume of [1-Bu-3-MeIm]BF₄ = 1 mL; volume of acetonitrile = 0.2, 0.4, 1 mL. (1) carbon glass electrode and (2) Pt electrode.

Electrolysis of C₄H₉SH in the [1-Bu-3-MeIm]BF₄ medium in the presence of toluene led to the appearance of a new peak of oxidation at the potential of 2.4 V (Fig. 4). The values of current for the peaks of oxidation of the substrate and the reagent during electrolysis decreased, indicating their consumption during the electrochemical reaction. The yield with respect to current was of 38%. The products of electrolysis were identified by electrochemical method, the IR spectroscopy data, and chromatography on capillary column with ionic liquid.

Scheme 1.



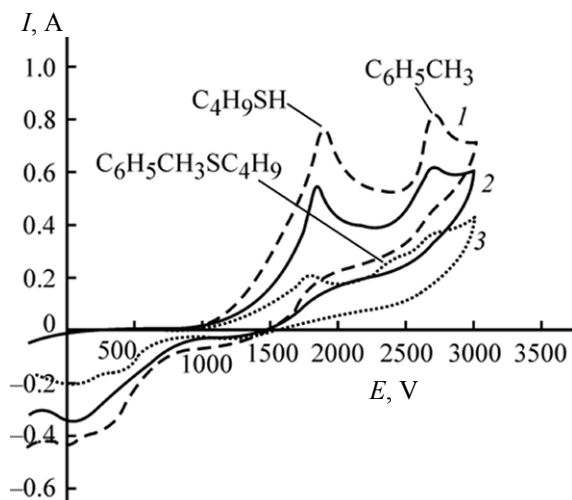
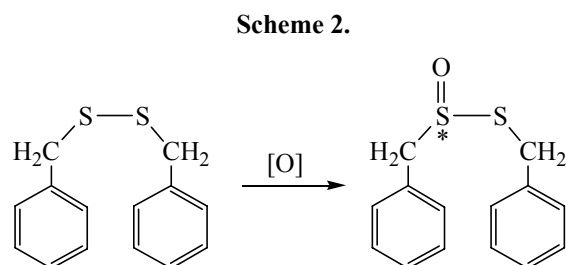


Fig. 4. Cyclic voltamperograms for electrolysis of C_4H_9SH in the presence of toluene in the medium $[BuPy]BF_4-CH_3CN$ (1 : 1) ($v = 200$ mV/s, Ag/AgCl, $c = 5 \times 10^{-3}$ mol/L, Pt electrode). (1) before electrolysis, (2) after 7 min, and (3) after 17 min.

Similar reactions were slower in acetonitrile or methylene chloride in the presence of background electrolyte, so that 75% conversion of the thiol was attained only after 1–2 h of electrolysis. The use of ionic liquids reduced the time of electrolysis by approximately 3 times. The observed acceleration of the reaction was caused by the ability of the ionic liquid to distribute the compound uniformly over the whole volume, coordinating the reagent in the position favorable for the reaction. Unlike polar molecular solvents, ionic liquids provide a unique micro-surrounding for the compounds, preserving their high catalytic activity [13].

The diversity of properties of ionic liquids allows elaboration of the combined processes including the extraction and subsequent reactions of the extracted sulfur-containing components with organic substrates. Taking into account the examined electrochemical reactions, the proposed combined process of the



synthesis of aromatic sulfur compounds could be represented by the Scheme 3.

The scheme describes the mechanism of interaction of a model fuel (based on heptane and butanethiol) with ionic liquid and further involvement of the extracted sulfur impurities in the organic synthesis.

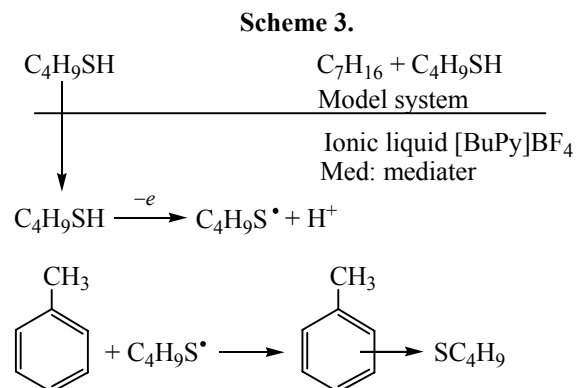
In summary, the electrochemical properties of the pyridinium and 1-butyl-3-methylimidazolium salts as well as electrochemical transformations of C_4H_9SH and $C_6H_5CH_2SH$ in the ionic liquid medium $[1-Bu-3-MeIm]PF_6$, have been investigated in the present work, and the electrolysis of butanethiol in $[1-Bu-3-MeIm]BF_4$ was performed in the presence of toluene.

EXPERIMENTAL

Compound **1** was prepared via the procedure described in [14, 15]; compounds **2–5** were commercial products (Sigma Aldrich).

Preparative electrolysis was performed on stationary platinum planar electrodes (700 mm²) in a diaphragm-free three-electrode 100 mL cell. The oxidation potentials were measured using the method of cyclic voltammetry in a three-electrode cell system using an Ametek VersaSTAT 3 potentiostat with a working Pt electrode ($S = 3.14$ mm²), auxiliary Pt electrode ($S = 70$ mm²), and reference Ag/AgCl/KCl electrode, equipped with waterproof diaphragm.

Gas chromatography analysis of the sulfur compounds was performed using a Crystal Lux 4000 chromatograph equipped with a flame photometric detector and an SLB-IL111 capillary column (15 m \times 0.1 mm, 0.08 μ m) using 1,5-di(2,3-dimethylimidazolium)pentane-bis(trifluoromethylsulfonyl)imide as the active phase (ionic liquid). Ionic liquids were regenerated by stepwise or fractional re-extraction



using 10-fold volume of acetonitrile at 70°C and 70 mBar pressure. The time of single extraction cycle was 1–2 min.

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