## CHEMISTRY ===

# Redox Mediators of Hydrogen Sulfide Oxidation in Reactions with Cycloalkanes

N. T. Berberova<sup>a</sup>, E. V. Shinkar'<sup>a</sup>, I. V. Smolyaninov<sup>a, b</sup>, and K. P. Pashchenko<sup>a</sup>

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Abstract—An indirect electrochemical method for thiolation of cycloalkanes  $C_5-C_7$  has been suggested. The method is based on a new approach to activation of hydrogen sulfide by redox mediators. DOI: 10.1134/S0012500815120058

In recent years, there has been an increasing trend toward using electrosynthesis as one of the "green chemistry" methods for production of various valuable organic compounds. Replacement of toxic reagents by electric current enables the in situ generation of reactive intermediates, which is favorable for carrying out reactions under relatively mild conditions and makes the process more environmentally friendly [1].

Much attention focuses on the search for the ways to reduce the electrode overvoltage in the course of electrosynthesis. To solve this problem, indirect electrosynthesis is increasingly often used where heterogeneous electron transfer between the electrode and the substrate is replaced by a homogeneous reaction of the reagent (substrate) with the mediator generated at a lower potential. Among the advantages of mediators is also their ability for regeneration at the electrode, which makes it possible to use them in catalytic amounts [2]. Inorganic mediators have been rather well studied [3]; however, little is known about their reactions with hydrogen sulfide.

We have demonstrated that direct electrooxidation of  $H_2S$  in reactions with unsaturated and aromatic hydrocarbons leads to the quantitative formation of organic sulfur compounds [4, 5]. In [6, 7], the authors have studied the possibility of using mediators based on triarylamines and metal complexes with redoxactive organic ligands to synthesize aliphatic thiols, sulfides, and disulfides widely applied in industry and agriculture [8].

e-mail: berberova@astu.org

Recent studies have shown that anodic activation of hydrogen sulfide in the presence of cyclopentane proceeds at a rather high oxidation potential of  $H_2S$  in dichloromethane (1.70 V) and leads to the formation of substrate thiolation products at room temperature [9].

The aim of the present work was to study the possibility of using redox mediators for indirect  $H_2S$  activation in the reaction with inert cycloalkanes at lower anodic potential values.

The following redox pair were considered as  $H_2S$  oxidation mediators:  $Br^-/Br^{\bullet}$  (tetrabutylammonium bromide) (**I**);  $QH_2/Q$  (3,5-di-*tert*-butyl-1,2-dihydroxy-benzene/3,5-di-*tert*-butyl-*o*-benzoquinone) (**II**).

Commercially available mediators-tetrabutylammonium bromide (Aldrich, 98%), 3,5-di-tert-butyl-obenzoquinone (Fluka, 98%), and 3,5-di-tert-butyl-1,2-dihydroxybenzene (Fluka, 98%)—were used. Electrochemical measurements were carried out with an IPC-Pro potentiostat at a Pt anode in CH<sub>2</sub>Cl<sub>2</sub> in the presence of 0.1 M n-Bu<sub>4</sub>NClO<sub>4</sub>. Microelectrolysis of an H<sub>2</sub>S –cycloalkane mixture was carried out with the use of a PI-50.1 potentiostat in potentiostatic mode at a potential of 1.04 V (redox mediator I) or 1.45 V (redox mediator II). The reference electrode was a saturated silver chloride electrode (Ag/AgCl/KCl) with a waterproof diaphragm. Chromatographic analysis of the synthesized organic sulfur compounds was performed on a Kristall-Lux 4000M gas chromatograph with a flame photometric detector. The IR spectra were recorded on an FSM 1201 FT spectrophotometer (400–5000 cm<sup>-1</sup>); chromatography/mass spectra were recorded on an Agilent Technologies 6890N GC System equipped with an Agilent Technologies 5973N MSD mass-selective detector. X-ray fluorescence analysis was carried out on an ASE-1 energy dispersive sulfur analyzer. Quantum-chemical calculations were

<sup>&</sup>lt;sup>a</sup> Astrakhan State Technical University, ul. Tatishcheva 16, Astrakhan, 414056 Russia

<sup>&</sup>lt;sup>b</sup> Toxicology Research Group, Southern Scientific Center, Russian Academy of Sciences, ul. Tatishcheva 16, Astrakhan, 414025 Russia

performed with the Gaussian 03 program by the density functional theory method (B3LYP, 6-31++G(d,p)) basis set). The solvent effect was considered using the polarized continuum model (PCM).

The thiyl radical was generated from  $H_2S$  by using selected redox mediators at room temperature by Scheme 1:



Scheme 1.

The electrochemical oxidation of redox mediators proceeds at the anodic potential 0.92 V for Br<sup>-</sup>/Br<sup>•</sup> and 1.24 V for QH<sub>2</sub>/Q. The Br<sup>-</sup>/Br<sup>•</sup> redox pair activates H<sub>2</sub>S to an unstable radical cation through electron transfer, whereas *o*-benzoquinone (Q), a product of oxidation of 3,5-di-*tert*-butyl-1,2-dihydroxybenzene (QH<sub>2</sub>), plays the role of the dehydrogenating agent with respect to H<sub>2</sub>S.

The dimerization of thiyl radicals leads to disulfane (0.3 V), and its oxidation under electrolysis conditions leads to a further growth of the sulfide chain with subsequent conversion of linear polysulfanes ( $H_2S_n$ , n = 2-8) into sulfur (-1.20 V) [5]. Unlike  $QH_2/Q$  [10, 11], redox pair I has not been considered earlier by us. As the reagent concentration increases, the reaction of redox pairs I and II with hydrogen sulfide leads to an increase in the anodic peak current of the mediator, which is evidence of the catalytic effect in the course of the electrochemical process.

The possibility to generate thiyl radical at room temperature with the use of redox mediators was studied for their reactions with unsubstituted and alkyl-substituted cycloalkanes  $C_5-C_7$ . The reactions proceed through a series of successive stages by the radical mechanism (Scheme 2), which leads to the formation of a mixture of reaction products in an anaerobic medium: cyclic thiols (RSH), disulfides (RSSR), and trisulfanes (RSSSR).



At the first stage, a hydrogen atom is eliminated from cycloalkane with subsequent recombination of the cycloalkyl and thiyl radicals. This leads to cycloalkanethiols, which are oxidized to the corresponding disulfides in the presence of redox mediators I and II. Chemical oxidants of different strength or an anode are applied to synthesize organic tri- and tetrasulfanes [12, 13]. In all of these reactions, direct oxidation of H<sub>2</sub>S leads to cyclooctasulfur as a side product, whatever the nature of substrates and redox mediators. The presence of S<sub>8</sub> among the reaction products causes the growth of the sulfide chain in RSSR to give trisulfanes. The current yield and composition of the reaction products can be changed by varying the hydrogen sulfide-to-cycloalkane concentration ratio. The increase in H<sub>2</sub>S content promotes preferential formation of trisulfanes through disproportionation of tetra- and pentasulfanes.

The results of the reactions of  $H_2S$  with cycloalkanes with the use of redox pairs I and II are presented in the table. In the series of unsubstituted cycloalkanes  $C_5-C_7$ , the overall yield of organosulfur reaction products depends on the type of redox mediator; in this context, redox pair I is most promising.

For redox pair **I**, with increasing the ring size of unsubstituted cycloalkanes, the yield of corresponding cycloalkanethiols and disulfides increases while the thiol/trisulfane ratio decreases; for the initial hydro-carbons, this ratio is 2.8 for C<sub>5</sub>, 2.2 for C<sub>6</sub>, and 1.9 for C<sub>7</sub>. With an increase in the ring size of the C<sub>5</sub>–C<sub>7</sub> substrates, the ratio of the forming cycloalkanetiols changes from 1 to 4.3 and for trisulfane, from 1 to 2.6, which points to the decrease in the probability of further transformations of thiols for larger hydrocarbon rings.

When redox mediator I is used, the presence of alkyl substituents in cyclohexane has little effect on the overall yield of organic sulfur derivatives (table). For cyclohexane and its alkyl-substituted derivatives, the yield of thiols is almost independent of the substituent nature (4.3-5.2%). Secondary transformations of cyclohexanethiols leads to disulfide and then to trisulfanes in the presence of elemental sulfur; their overall yield varies within 16.5-18.8%. This fact confirms that the reactivity of cycloalkanethiols depends on the ring size. The decrease in the yield of S<sub>8</sub> as compared with unsubstituted cycloalkanes is evidence of the

preferential content of trisulfanes in the mixture of reaction products.

With redox mediator II, the reactions of cycloalkanes  $C_5-C_7$  yield thiols (2.5–6.7%) and disulfides (5.0–8.3%), while trisulfanes are absent among the reaction products, which is caused by the inertness of the generated *o*-quinone toward disulfides. Generation of organic trisulfanes is typical of methyl- and ethylcyclohexane, which is due to the direct electrochemical oxidation of the resulting disulfides (1.48– 1.50 V) at the anode under the electrolysis conditions.

When redox pair I is used, bromide ion is oxidized to atomic bromine capable of reacting with both H<sub>2</sub>S and cycloalkanes. This is responsible for the possibility of an alternative stage of generation of the cycloalkyl radical through the Br radical attack at the substrate, which leads to an increase in the yield of sulfur-containing products as compared with the reactions in the presence of redox mediator II. The reactivity of the selected substrates in the presence of redox mediator I is independent of the ring size (decreases only slightly in the series  $C_7 > C_6 > C_5$ ), which correlates with quantum-chemical calculation results. From the thermodynamic standpoint, the probability of the cycloalkyl radical being generated by the attack of the thiyl radical is comparable for the  $C_5-C_7$  cycloalkanes, and the heat ( $\Delta H$ ) of this stage varies within 35.7–45.7 kJ/mol.

According to quantum-chemical calculations, in the reaction of H<sub>2</sub>S with cycloalkanes in the presence of redox mediator I, the thermodynamic probability of H<sub>2</sub>S dehydrogenation ( $\Delta H = -18.5 \text{ kJ/mol}$ ) is higher than the probability of elimination of a hydrogen atom from the substrate ( $\Delta H = 17.3-27.2 \text{ kJ/mol}$ ). Redox mediator I is active to thiols according to the experimental electrochemical data and calculated heats of formation of cycloalkylthiyl radicals ( $\Delta H = -33.5 \dots$ -27.1 kJ/mol).

The cycloalkyl radical is generated only by the attack of the thivl radical at the substrate when redox pair II is used. This leads to a decrease in the overall vield of organosulfur reaction products as compared with the activation of the reagent by redox pair I. In the presence of redox mediator II, cyclohexane turns out to be thermodynamically most stable. This is consistent with the data on the reactions of  $H_2S$  with the  $C_5-C_7$  cycloalkanes carried out under conditions of direct anodic activation of the reagent and is associated with the negligible ring strain for cyclohexane. The reaction with methylcyclohexane leads to the highest yield of disulfide, trisulfane, and molecular sulfur. The accumulation of S<sub>8</sub> in sufficient amounts in the course of reaction also promotes the formation of organic polysulfanes. In the reactions of the  $C_5-C_7$ cycloalkanes with hydrogen sulfide (table), there is no

Yields of sulfur-containing organic compounds and molecular sulfur in reactions of  $H_2S$  with  $C_5-C_7$  cycloalkanes in the presence of redox mediators I and II

	Ι		II	
Substrate	current yield of reaction products, %	current yield of $S_8$ , %	current yield of reaction products, %	current yield of $S_8$ , %
Cyclopen- tane	12.7	42.0	10.0	27.0
Cyclohexane	22.8	40.0	7.5	33.5
Cyclohep- tane	51.5	28.0	15.8	29.5
Methylcy- clohexane	25.3	22.2	32.7	35.8
Ethylcyclo- hexane	23.8	23.7	25.5	22.5

noticeable effect of the substrate nature on the oxidation of  $H_2S$  and  $H_2S_n$  to  $S_8$ , since the yields of sulfur in all the reactions are comparable. The observed tendency is explained by the high propensity of the thiyl radical to dimerize into disulfane and inorganic polysulfanes. The introduction of alkyl groups into the ring leads to the increase in the yield of sulfur compounds, which is evidently due to the possibility of thio substitution reactions in the side group of the substrate.

The yield of sulfur for the Br<sup>-</sup>/Br<sup>•</sup> redox pair is higher as compared with that for  $QH_2/Q$ , which is explained by the higher regeneration rate of the mediator owing to the absence of an additional chemical stage (deprotonation) in the catalytic cycle of redox transformations.

The content of organosulfur compounds obtained in the reaction of hydrogen sulfide with cycloalkanes also depends on the substrate nature and the type of redox mediator (figure).

According to the figure, redox pair II turned out to be more efficient in the reaction of methylcyclohexane with  $H_2S$ , since the overall yield of sulfur-containing products is the highest one at comparable disulfide, thiol, and trisulfane contents.

In electrolysis in the presence of redox mediator I, its concentration decreases by 10%, as distinct from QH<sub>2</sub>/Q. The insignificant consumption of redox mediator I is caused by the inevitable formation of hydrogen bromide at the stage of substrate dehydrogenation in the presence of atomic bromine. However, brominated derivatives of the substrate are absent among the products of electrolysis of an H<sub>2</sub>S–cyclohexane mixture in the presence of redox mediator I. This fact is consistent with the results of the photooxygenation reaction of cyclohexane in the presence of



Yield of organosulfur compounds as a function of the type of redox mediator used (I or II) for the reaction hydrogen sulfide with methylcyclohexane.

the  $Cl^{-}/Cl^{\bullet}$  redox pair, which is, like the selected  $Br^{-}/Br^{\bullet}$  redox mediator, was not involved in transformations with the substrate [14].

Thus, we have suggested an indirect electrochemical method of thiolation of the C<sub>5</sub>–C<sub>7</sub> cycloalkanes. The method is based on a new approach to activation of hydrogen sulfide by redox mediators I and II. To reduce the anodic overvoltage of the H<sub>2</sub>S oxidation, the Br<sup>-</sup>/Br<sup>•</sup> and QH<sub>2</sub>/Q redox pairs have been used ( $\Delta E(I) \approx 0.76$  V;  $E(II) \approx 0.35$  V), which makes it possible to generate the thiyl radical under mild conditions. The electrosynthesis under energetically favorable conditions leads to a mixture of organic sulfur compounds: cycloalkanethiols, disulfides, and organic trisulfanes. The developed one-step synthesis of valuable sulfur-containing substances opens prospects for improving the known methods of their production by reducing the environmental and energy constraints.

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