

PAPER • OPEN ACCESS

Arenothiophenes in oil basic sulfoxides synthesis and oxidation receiving sulfoxides from oil

To cite this article: L Sh Bozorova *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **939** 012018

View the [article online](#) for updates and enhancements.

You may also like

- [Molybdenum compounds in organic synthesis](#)
Ravil I. Khusnutdinov, Tatyana M. Oshnyakova and Usein M. Dzhemilev
- [Rotor film reactor](#)
L R Gainullina, V P Tutubalina and L S Sabitov
- [Investigation of DESO/LIPID membranes interaction by X-Ray scattering](#)
Yu E Gorshkova, O I Ivankov, A I Kuklin et al.

Arenothiophenes in oil basic sulfoxides synthesis and oxidation receiving sulfoxides from oil

L Sh Bozorova^{1*}, M J Qurbanov², O J Pirimov¹, and O Tursunov^{3,4,5}

¹Karshi branch of Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, 180100 Karshi, Uzbekistan

²Karshi State University, 180100 Karshi, Uzbekistan

³Department of Power Supply and Renewable Energy Sources, Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, 100000 Tashkent, Uzbekistan

⁴Research Institute of Forestry, 111104 Tashkent, Uzbekistan

⁵Gulistan State University, 120100 Gulistan, Uzbekistan

*Email: bozorovalobar26@gmail.com

Abstract. Some of the sulfide compounds were converted to sulfoxides by the action of a 30% solution of hydrogen peroxide on the acid catalyst of a molecule of bicyclic sulfide organic compounds in the paraffin distillate of the oil. The resulting sulfoxides were treated with 70% sulfuric acid and sulfate compounds of sulfoxides were obtained. In order to confirm the composition and structure of these compounds, chemical reactions of the corresponding sulfoxides on the basis of benzothiophene derivatives were carried out.

1. Introduction

As we all know, saturated hydrocarbons are now the main raw material of many industrial enterprises. It should be noted that the main source of saturated hydrocarbons is natural oil and gas. The oil and gas industry in Uzbekistan is one of the main and leading sectors of the economy. Kashkadarya region of Uzbekistan is a leader in oil and gas production.

Representatives of cyclic sulfur compounds in oil are now widely used in various sectors of the economy. In particular, among a large number of organic compounds, sulfur-containing organic compounds have been used as potent drugs, surfactants, semiconductors, compounds with optical memory properties, and as good inhibitors of acid corrosion [1-6]. The largest reserves of organic sulfur compounds are petroleum raw materials, which can be used for various purposes and a variety of drugs [7].

Sulfoxides are key intermediates in the production of a variety of physiologically active compounds [8, 9]. The oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides [10]. The oxidation of sulfides is a fundamental process that produces sulfoxides in one of the most straightforward ways. In the most typical sulfoxidation reactions, a variety of reagents are utilized, including peracids and halogen derivatives. However, many environmentally undesirable byproducts and low oxygen atom efficiency are prevalent problems in these common reactions [11, 12]. In recent green chemistry endeavors, the discovery of environmentally benign catalysts [13] and oxidants has become a research hotspot. A variety of catalytic systems, including metal-containing catalytic systems [14-16], metal-free protocols, and biocatalysts in the presence of various oxidants [17, 18, 19], have been developed over the last decade for their preparation.

While there has been significant development in this field, selective production of sulfoxides remains a key difficulty since sulfoxides are frequently overoxidized to sulfones. Furthermore, the published techniques include flaws such as complex catalytic systems that require an excess of catalyst or oxidant,



as well as low yields and selectivities [11, 20]. Aqueous hydrogen peroxide is generally considered one of the most environmentally benign "green oxidants" because it is inexpensive, readily available, has high effective oxygen content, is safe in operation and storage, and yields stoichiometric amounts of environmentally friendly water as a byproduct [21]. Because of these properties of aqueous hydrogen peroxide, numerous useful methods for oxidizing sulfides to sulfoxides and sulfones with various transition metal and acid catalysts have been developed.

2. Materials and Methods

Synthesis of 5-Acetyl-S-dibromo-1-tain

We equip a three-tube volumetric flask with a volume of 50 ml with a mechanical stirrer, a dropper funnel and an inverted refrigerator. Add 2 g (0.0112 mol) of 5-acetyl-1-thiaindane and 5 ml of carbon (IV) chloride to the flask. Cool the flask from the outside to 0 °C and add 1.76 g (0.011 mol) of bromine in 5 ml of carbon (IV) chloride drop by drop. The reaction mixture in the flask was stirred at 200C for 2 h. The mixing was then stopped and calmed. Sediment is formed. The precipitate formed was filtered from 5-Acetyl-S-dibromo-1-taine. Twice washed in 10 milliliters of carbon (IV) chloride. Vacuum dried. the yield of the reaction is 85%. Liquidus temperature 54-55 °C.

5-Acetyl-S-dibromo-2-methyl-1-tiaindan

The reaction was carried out by the same method of synthesis from the above 5-Acetyl-S-dibromo-1-taine. For the reaction, 2 g (0.01 mol) was obtained from 5-acetyl-2-methyl-1-thiaine. The yield of the reaction product is 68%. Liquidus temperature 69-70 °C.

5-Acetyl-1-taindansulfoxide (I)

Put 2 g of 5-acetyl-S-dibromo-1-taidan in a small beaker. At room temperature we add 20 ml of water to the substance in this glass. Stir this mixture in a magnetic bowl for 1 hour. We then extract the product in the beaker using ether. We dehydrate the ether layer using magnesium sulfate. Then we drive the broadcast. The crystals fall. Product yield is 95%. Liquidus temperature 82-83 °C.

5-Acetyl-2-methyl-1-taindansulfoxide (II)

The reaction was carried out as the above 5-acetyl-1-taindansulfoxide synthesis method. For the reaction, 2 g of 5-acetyl-S-dibromo-2-methyl-1-thiaine was obtained. product yield is 90%. Liquidus temperature 35-36 °C.

3. Results and Discussions

In this regard, based on the above data, we also convert bicyclic sulfur organic compounds in the oil of Eshankuduk oil field in our region into sulfoxides by oxidation and chemical synthesis of bicyclic sulfur organic compounds found in natural oil and their conversion into sulfoxides. found it necessary to study the structure. Let us briefly dwell on the Eshankuduk oil field.

The Eshankuduk oil field is located in the southern part of the Beshkent region, and oil samples were taken from №3 wells belonging to this field at a depth of 3720-3800 meters. The parameters of this well oil are given in the Table 1 below, in which the average density of oil is 862.6 kg / m³, and the amount of sulfur is 1.92%. The content of tar in oil is -3.84%, asphaltenes -1.12% and paraffins 2.96%. The viscosity of the oil at 20 °C is 31.40 mm² / s, and the viscosity at 50 °C is 11.16 mm² / s. shankuduk oil is a medium-weight oil with sulfur, resin and paraffin. The physicochemical analysis of Eshankuduk oil was carried out by the staff of Oil and Gas Geochemistry (IGIRNGM).

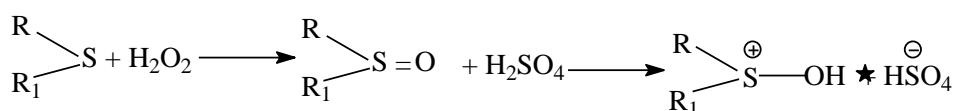
Table 1 below provides a physicochemical description of Eshankuduk oil.

We also used the method of action of various oxidants in the separation of representatives of long radicals in the side chain of arenothiophenes in the Eshankuduk oil field, one of the oil fields of our region, and separated the reaction products in the form of sulfoxides and sulfonides of these substances. In order to enrich the sulfur aromatic compounds, the mixture was treated under the catalyst of 30% hydrogen peroxide acid and then converted to the corresponding sulfonic compounds. Bicyclic sulfide organic compounds in oil differ from other sulfide compounds in terms of their specific electronic structures and physicochemical properties. Therefore, when a kerosene distillate of oil is treated with a 30% solution of hydrogen peroxide in an acid catalyst, some of the sulfide compounds in the oil are converted to sulfoxides, respectively. When the resulting sulfoxides are treated with 70% sulfuric acid, the oxygen

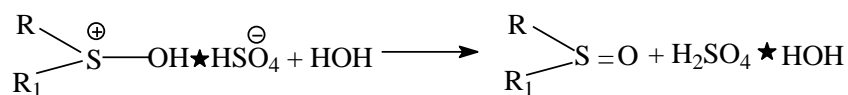
atom in the sulfoxide molecule protonates at the expense of its vacant electrons and forms the sulfate compounds of the sulfoxide compounds formed accordingly.

Table 1. Eshankuduk (№ 3 wells) field oil physicochemical description

Indicators	Quantity
Density 20 °C, kg/m ³	862.6
Molecular mass g / mol	231.0
Kinematic viscosity:	
20 °C at room temperature	31.40296
50 °C at room temperature	11.16348
Ignition temperature, °C	27.0
Freezing point, °C	-15.0
Saturated vapor pressure, мм.с.у.с., Па.	96.2 /12823.5
37,8 °C at room temperature	138.4 /18448.7
50,0 °C at room temperature	
Composition,% by weight:	
sulphur	1.92
asphaltenes	1.12
silicagel resin	3.84
paraffins	2.96
oil	42.67
water	1.10
mechanical additions	0.245
Number of acids, mg KOH for 1 g of oil	0.2904
Coking,%	3.0311
Density,%	0.0183
Fractional yield,%: (relative to mass)	
200 °C at room temperature	14.17
300 °C at room temperature	33.00
350 °C at room temperature	54.85



Sulfate complexes of the obtained sulfoxides are transferred from the sulfides and hydrocarbons of the unoxidized oil as a result of interfacial separation in the reaction mixture to a solution of sulfuric acid. The sulfuric acid layer in the mixture is then separated and treated with a 10% solution of sulfuric acid. As a result of the decomposition of the sulfoxide-sulfate complex formed above, the sulfoxides rise to the top of the solution. The dilute sulfuric acid, on the other hand, decomposes into the lower layer of the mixture.

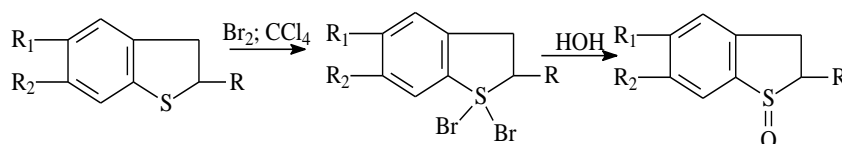


We performed the following reactions in order to obtain appropriate sulfoxides by chemical synthesis of benzothiophene derivatives, one of the naturally occurring arenothiophene compounds in the oil. Molecules of benzo [b] thiophene derivatives 5-acetyl-1thian and 5-acetyl-2-methyl-1-thiaine were reacted with molecular bromine in a tetrachloromethane medium without the presence of a catalyst. The reaction was carried out at a temperature of 20 °C for 2 hours at the equivalent ratios of the reactants. As a result of the reaction, the formation of blue crystalline substances was observed, and the decomposition of this substance under the influence of water was observed. Table 2 highlights the overall description of petroleum sulfoxide.

Table 2. Description of petroleum sulfoxides

Product name	productivity		Mr, g	Element composition		Sulfide,%		Sulfide oxide,%	$\frac{20}{n_D}$
	g	%		C	H	first	In the faction		
Oxidized Oil	200	100	194	84	13	0.80	100	1.1	1.500
Extract	13.6	6.3	202	68.2	11.1	-	-	12.6	1.520
Refined	180	91	-	-	-	0.66	91	0.018	-
Washed Extract Product	2.1	0.86	-	-	-	-	-	1.0	-
Sum	200.1	98.3	-	-	-	-	-	92	-

The study of the reaction results showed that the interaction of thiamine acyl derivatives with molecular bromine resulted in the formation of S-dibromo derivatives, and its decomposition with water easily resulted in the formation of sulfoxides of acetylthiene, respectively. The scheme of this reaction can be explained as follows:



I. R=H; R₁= CH₃CO; R₂=H; II. R= CH₃; R₁= CH₃CO; R₂=H;

The S-dibromosides formed as a result of the reaction can be explained by the fact that in reactions without the presence of catalysts in the tetrachloromethane solution, the sulfur atom in the molecule reacts due to its vacant pair of electrons, resulting in stable S-dibromo derivatives of acetyl-1-thianides. From the interaction of these S-dibromo compounds with water, 5-acetyl-1-thiaindensulfoxide (I) and 5-acetyl-2-methyl-1-thiaindensulfoxides (II) were obtained, respectively.

The data in the table show that the hydrolysis of the product of the bromination reaction of molecular bromine with acetylthiene and its derivatives in tetrachloromethane solution results in the formation of high-yielding sulfoxides.

Table 3 below shows the physicochemical characteristics of acetylthiene sulfoxides.

IR-spectral analysis of the obtained sulfoxides showed that the absorption lines in the 1060–1055 cm⁻¹ area had intensive absorption lines belonging to the sulfoxide group. In addition, the intensive absorption lines of the unsaturated bond belonging to the carbon-carbon bond in the benzene ring give their absorption lines in the 1600 cm⁻¹ area, while the non-plane deformation oscillations of the CH bonds in the benzene ring appear in the 838-835 cm⁻¹ area. The plane deformation oscillations of the CH bonds in the benzene ring are in the 900 cm⁻¹ region, the absorption lines characteristic of the carbonyl group are strongly intense in the 1690 cm⁻¹ area, and the C-S-C bond oscillations in the molecule are in the 1060 cm⁻¹ area. Table 4 below shows the IR-spectrum data relating to these sulfoxides.

Table 3. Physicochemical characterization of acetyl-1-thiaindensulfoxides

product	productivity, %	liquid temperature °C.	Found, %.			Brutto formula	Calculated, %.		
			C	H	S		C	H	S
I	95	82-83	61.92	5.26	16.68	C ₁₀ H ₁₀ O ₂ S	61.64	5.19	16.50
			61.88	5.18	16.58				
II	90	35-36	63.56	5.92	15.51	C ₁₁ H ₁₂ O ₂ S	63.45	5.81	15.39
			63.51	5.86	15.46				

It is possible to separate organic compounds of sulfur in oil, to determine their structure and composition, to synthesize high-molecular-weight representatives found in oil using synthetic methods based on the obtained results. The synthesized substances allow their natural representatives not only as standard drugs, but also to study the physicochemical, chemical, physiological, anticorrosion, surfactant and other specific properties of ore beneficiation and to explore new areas of application of sulfur organic compounds in oil.

Table 4. Characteristic absorption lines in the IR spectrum of acetyl-1-thiaindensulfoxides

Chemical bonds in a molecule	Product cm^{-1}	
	I	II
In the benzene ring C=C	1600	1600
Non-plane deformation vibrations of CH bonds in a benzene ring	838	835
Plane deformation oscillations of CH bonds in a benzene ring	900	900
		925
The carbonyl group in the molecule is a C = O bond	1690	1690
Sulfoxide bond in the molecule, C = O oscillations	1060	1060
C-S-C bond oscillations in the molecule	740	720

References

- [1] Usmanov UR, Inoyatov NO, Usmanov R, Kukaniev MA 2009 Influence of some synthetic aromatic and semi-aromatic compounds on corrosion of steel and hydrochloric acid *Report of the Academy of Sciences of the Republic of Tajikistan* **52** 30-35.
- [2] El-Dien B, El-Gendy M, Atwa ShT, Ahmed AA, El-Etre AY 2019 Synthesis and Characterization of Carbon Steel Corrosion Inhibitors Based on 4,5,6,7-tetrahydrobenzo [b] thiophene Scaffold. Physicochemical problems of materials protection *Protection of Metals and Physical Chemistry of Surfaces* **55** 179–186.
- [3] Liger F, Bouhours P, Ganem-Elbaz C, Jolivald C, Pellet-Rostaing S, Popowycz F, Paris JM, Lemaire M 2016 C2 Arylated Benzo[b]thiophene Derivatives as Staphylococcus aureus NorA Efflux Pump Inhibitors *ChemMedChem* **11**(3) 320-330.
- [4] Raxmatova GB, Kurbanov MJ, Atakulova DD 2020 Bromirovaniya atsilproizvodnyx 1-tiaindanovogo ryada, *International Conference on Europe Science*, Praha, Czech Republic.
- [5] Borisenkova SA, Vildanov AF, Mazgarov AM 1995 Modern problems of oil observation of oil and oil products *Russian Journal of Chemistry* **39** 5.
- [6] Lukyanov IP, Basistov AG 1974 Chemistry of seroorganic compounds in petroleum and petroleum products, Gostorgtexizdat, Moscow.
- [7] Sadare OO, Obazu F, Daramola MO 2017 Biodesulfurization of Petroleum Distillates—Current Status, Opportunities and Future Challenges *Environments* **4**(4) 85.
- [8] Francioso A, Conrado AB, Mosca L, Fontana M 2020 Chemistry and Biochemistry of Sulfur Natural Compounds: Key Intermediates of Metabolism and Redox Biology *Oxidative Medicine and Cellular Longevity* **2020** 8294158.
- [9] Zhang R, Ding H, Pu X, Qian Zh, Xiao Y 2020 Recent Advances in the Synthesis of Sulfides, Sulfoxides and Sulfones via C-S Bond Construction from Non-Halide Substrates *Catalysts* **10** 1339.
- [10] Golchoubian H, Hosseinpoor F 2007 Effective oxidation of sulfides to sulfoxides with hydrogen peroxide under transition-metal-free conditions *Molecules* **12**(3) 304-311.
- [11] Tong Q-L, Fan Zh-F, Yang J-W, Li Q, Chen Y-X, Cheng M-Sh, Liu Y 2019 The Selective Oxidation of Sulfides to Sulfoxides or Sulfones with Hydrogen Peroxide Catalyzed by a Dendritic Phosphomolybdate Hybrid *Catalysts* **9** 791.
- [12] Yang Ch, Jin Q, Zhang H, Liao J, Zhu J, Yu B, Deng J 2009 Tetra-(tetraalkylammonium) octamolybdate catalysts for selective oxidation of sulfides to sulfoxides with hydrogen peroxide *Green Chem.* **11** 1401-1405.

- [13] Tursunov O, Tilyabaev Z 2019 Hydrogenation of CO₂ over Co supported on carbon nanotube, carbon nanotube-Nb₂O₅, carbon nanofiber, low-layered graphite fragments and Nb₂O₅ *J Energy Institute* **92**(1) 18-26.
- [14] Tursunov O, Zubek K, Czerski G, Dobrowolski J 2020 Studies of CO₂ gasification of the *Miscanthus giganteus* biomass over Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter as catalysts *J Therm Anal Calorim* **139** 3481-3492.
- [15] Tursunov O, Kustov L, Tilyabaev Z 2019 Catalytic activity of H-ZSM-5 and Cu-HZSM-5 zeolites of medium SiO₂/Al₂O₃ ratio in conversion of n-hexane to aromatics *J Petroleum Science and Engineering* **180** 773-778.
- [16] Tursunov O, Zubek K, Dobrowolski J, Czerski G, Grzywacz P 2017 Effect of Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O Promoter Catalysts on H₂, CO and CH₄ Concentration by CO₂ Gasification of *Rosa Multiflora* Biomass *Oil & Gas Science and Technology – Rev. IFP Energies Nouvelles* **72**(6) 37.
- [17] Kananovich D, Elek GZ, Lopp M, Borovkov V 2021 Aerobic Oxidations in Asymmetric Synthesis: Catalytic Strategies and Recent Developments *Front. Chem.* **9** 614944.
- [18] Molina MA, Gascón-Pérez V, Sánchez-Sánchez M, Blanco RM 2021 Sustainable One-Pot Immobilization of Enzymes in/on Metal-Organic Framework Materials *Catalysts* **11**(8) 1002.
- [19] Garzón-Posse F, Becerra-Figueroa L, Hernández-Arias J, Gamba-Sánchez D 2018 Whole Cells as Biocatalysts in Organic Transformations *Molecules* **23**(6) 1265.
- [20] Ye C, Zhang Y, Ding A, Hu Y, Guo H 2018 Visible light sensitizer-catalyzed highly selective photo oxidation from thioethers into sulfoxides under aerobic condition *Sci Rep.* **8**(1) 2205.
- [21] Gogoi P, Kalita M, Bhattacharjee T, Barman P 2014 ChemInform Abstract: Copper-Schiff Base Complex Catalyzed Oxidation of Sulfides with Hydrogen Peroxide *Tetrahedron Letters* **55**(5) 1028–1030.