

Direct Electrochemical Synthesis of Bismuth (III) Thiulates/Dithiulates and Their Coordination Compounds

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Abstract: Bismuth (III) thiulates/dithiulates have been synthesized by electrochemical reactions of ethanethiol, 2-propanethiol, 2-methylpropane-2-thiol, Butanethiol, 1-pentanethiol, , Ethane- 1, 2-dithiol and Butane-1, 4-dithiol at sacrificial bismuth anode and inert platinum cathode using tetrabutylammonium chloride as supporting electrolyte. The coordination compounds of these thiulates/dithiulates with 1, 10-phenanthroline and 2, 2'-bipyridyl have also been synthesized electrochemically. The solid products that separated in the anode compartment have been isolated and characterized by elemental analysis and infrared spectral studies. Current efficiencies of these reactions are quite high.

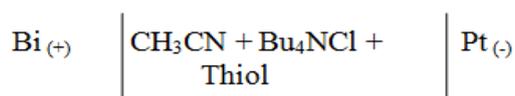
Keywords: H-type cell, electrochemical synthesis, Bismuth (III) thiulates/dithiulates, current efficiencies, sacrificial electrode.

I. Introduction

Electrochemical technique is the direct route to carry out oxidation or reduction without introducing any foreign oxidizing or reducing agent [1-3]. It has been used as synthetic method in organic chemistry [4-6] for last sixteen decades. In medical field, bismuth compounds are used to relieve diaper rash, treat burns as well as to treat gastric disorders such as diarrhea [7, 8]. Importantly these compounds are effective against bacterium, *Helicobacter pylori*, which causes peptic ulcers [9, 10]. In light of recent interest in the medicinal importance of bismuth compounds we are developing some simple compounds using electrochemical synthetic technique.

II. Experimental

Acetonitrile was kept over phosphorus pentoxide for 24 h and then double distilled. Freshly distilled acetonitrile was used as solvent in all these reactions. Tetrabutylammonium chloride (Reidal pure) was crystallized from conductivity water and dried under reduced pressure at 100° C. It was then used as supporting electrolyte in all these reactions. An H-type cell made of pyrex glass in which the cathode and anode compartments were separated from each other by a sintered glass disc of G-3 porosity, was used as the reaction vessel. Both compartments were provided with two openings; one for guard tube and the other for electrode. Platinum gauge (2.0x1.0x1.0 cm³) was used as cathode and bismuth rod (2.0x10.0x0.2cm³) as anode. Direct current was obtained with the help of Toshniwal electrophoresis power supply. The electrolytic solution in the anode compartment was stirred efficiently using magnetic stirrer. 1.0 mL of thiol, 1.0 g of tetrabutylammonium chloride and 250 mL of freshly distilled acetonitrile were taken in the H-type cell. Bismuth metal electrode was dipped in anode compartment and platinum gauge in the cathode compartment and outlets were sealed after fitting the guard tubes. Necessary connections were made with power supply and potential across the electrodes was then adjusted so that a current of 20 mA passed through the solution. The cell can be represented as:



Where:

Bi₍₊₎ is Bismuth anode.

Pt₍₋₎ is Platinum cathode.

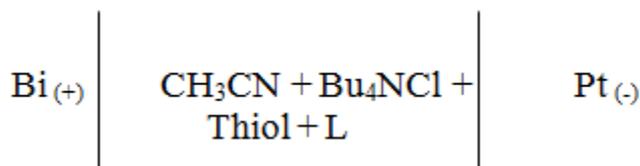
Bu₄NCl is supporting electrolyte.

The electrolysis was carried out with continuous stirring in the anode compartment. After conducting electrolysis for twelve hours, the product was filtered, washed with hot acetonitrile and dry ether and finally dried under vacuum. The current efficiencies (gram equivalents of metal dissolved per faraday of electricity passed) of all these reactions were determined by electrolyzing the above systems for exactly two hours at a constant current of 20 mA as reported earlier [3]. Melting point of all these products was recorded using electrical device with heating rate of 5° C per minute. Infrared spectra of the products were recorded on Perkin-Elmer spectrophotometer (RXI) in the region of 4000 – 450 cm⁻¹ using potassium bromide pellets. The products

were analyzed for bismuth contents. Weighed amount of the product was heated to dry mass with fuming nitric acid six times. The dry mass was dissolved in few drops of dilute nitric acid and 100 mL solution was made. The contents of bismuth in solution were estimated volumetrically by oxine method [11]. The microanalyses of C, H and S of these compounds have also been carried out.

2.1 The coordination compounds of bismuth thiolates and dithiolates

Bismuth thiolates and dithiolates were refluxed with 1, 10-phenanthroline or 2,2'-bipyridyl in different solvents like benzene, chloroform, carbon tetrachloride, DMSO, diethyl ether etc. for more than 48h. However, the elemental analysis shows that these donor molecules could not rupture the thiolate bridges in these compounds to form their coordination compounds. It was therefore decided to add the ligand to these thiolates and dithiolates before these are polymerized. Therefore in addition to supporting electrolyte, 1.0 g of the ligand has also been added to these systems and the solution was electrolyzed for 8h. The solid product separate in anode compartment was filtered, washed with dry ether and dried under vacuum. The analytical data conform to $\text{Bi}(\text{SR})_3 \cdot \text{L}$ in case of thiols and $\text{BiS}_2(\text{CH}_2)_n \cdot \text{L}$ in case of dithiols.



Where:

Bi (+) is Bismuth anode.

Pt (-) is Platinum cathode.

Bu₄NCl is supporting electrolyte

L is 1,10-phenanthroline or 2,2'-bipyridyl

III. Results and Discussion

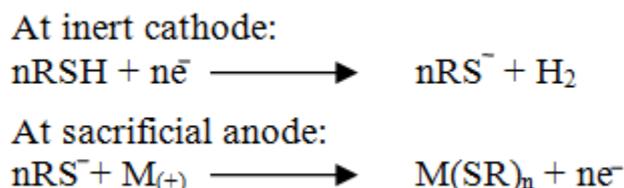
The products obtained from electrolysis of thiols in acetonitrile and tetrabutylammonium chloride are insoluble in commonly used organic solvents like chloroform, benzene, methanol, acetone, dimethyl sulphoxide, N, N-dimethyl formamide etc. All these compounds do not melt upto 300o C, however, colour of these compounds changes around 230o C thereby indicating that these products decompose around this temperature. The analytical data (bismuth, carbon, and hydrogen contents in all these products) along with their electrolytic characteristics of these systems are summarized in Table-I.

Table-I: Electrolysis Characteristics, Analytical and other Related Data of Electrolysis of Thiols at Bismuth Anode

System	Potential	Electricity Passed (Coulomb)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/Faraday)
					Bi	C	H	S	
Ethanethiol	40	864	C ₆ H ₁₅ S ₃ Bi	Pink	50.8 (53.3)	17.9 (18.3)	1.9 (3.82)	21.3 (24.4)	0.94
2- propanethiol	60	864	C ₉ H ₂₄ s ₃ Bi	Yellow	46.4 (48.0)	21.2 (24.8)	0.6 (4.83)	21.0 (22.1)	0.93
2-methylpropane-2-thiol	50	864	C ₁₂ H ₂₇ S ₃ Bi	Yellow	43.5 (43.9)	28.7 (30.2)	1.9 (5.6)	18.7 (20.1)	0.86
Butanethiol,	40	864	C ₁₂ H ₂₇ S ₃ Bi	Orange	41.0 (43.9)	31.0 (30.25)	4.3 (5.6)	18.6 (20.1)	0.87
1-pentanethiol	40	864	C ₁₅ H ₃₃ S ₃ Bi	Pink	39.1 (40.3)	33.3 (34.7)	55.5 (6.3)	17.2 (18.5)	0.96
Ethane- 1, 2-dithiol	50	864	C ₆ H ₁₅ s ₆ Bi	Purple	40.6 (42.8)	11.3 (14.7)	0.8 (3.1)	25.6 (39.3)	0.83
Butane-1, 4-dithiol	50	864	C ₁₂ H ₂₇ S ₆ Bi	Purple	34.8 (36.5)	21.6 (25.1)	0.6 (4.7)	31.3 (33.5)	0.84

Perusal of Table-I reveals that the analytical data conform to the molecular formula $\text{Bi}(\text{SR})_3$ and $\text{BiS}_2(\text{CH}_2)_n$. The infrared spectral data of these products reveals that the characteristic bands appear in the region of 559-530 cm⁻¹ and 530-470 cm⁻¹. However the band due to $\nu(\text{S-H})$ which generally appears around 2603-2499 cm⁻¹ is missing in the infrared spectra of these products. Survey of literature [12] reveals that $\nu(\text{M-S})$ stretching bands appear in the region of 400-250 cm⁻¹. The bands present in the region of 592-410 cm⁻¹ are attributed to $\nu(\text{Bi-S})$ stretching vibration [13, 14] of bridged metal thiolate and dithiolate indicating the polymeric nature of these compounds. The bands which are appearing in the region of 692-659 cm⁻¹ are also in agreement with the $\nu(\text{C-S})$ stretching modes reported in literature [15, 16]. The insoluble behavior of these

compounds in various organic solvents also supports the polymeric nature of these compounds. Current efficiencies of some of these systems have also determined which are quite close to 100% thereby indicating that the reactions leading to the formation of these thiolates and dithiolates are the predominant reactions of these systems. The reaction scheme for the formation of products is detailed below:



Survey of literature reveals [17] that $\nu(\text{C-N})$ in 1,10-phenanthroline or 2,2'-bipyridyl appear around 1310-1360 cm^{-1} . It has been observed that in these complexes these bands appear at 1600-1585 cm^{-1} higher than 1,10-phenanthroline or 2,2'-bipyridyl. Infrared spectra of these compounds also exhibit peaks in the region of 695-657 cm^{-1} , 578-558 cm^{-1} and 472-428 cm^{-1} [18]. These bands are assigned to $\nu(\text{C-S})$, $\nu(\text{Bi-S})$ terminal and $\nu(\text{Bi-S})$ bridged stretching vibrations respectively. Shift of these bands indicates that the ligand has been added to these systems. These coordinate compounds are also insoluble in commonly used organic solvents like benzene, methanol, acetone, dimethyl sulphoxide, N, N-dimethyl formamide etc thereby indicating that these could be polymeric in nature like their parent bismuth thiolate/dithiolate.

Table-II: Electrolysis Characteristics, Analytical and other Related Data of Electrolytic product of various thiol Systems + 1, 10-phenanthroline at Bismuth Anode

System	Potential	Electricity Passed (Coulomb)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/ Faraday)
					Bi	C	H	S	
Ethanethiol +1,10-phenanthroline	40	864	$\text{C}_6\text{H}_{15}\text{S}_3\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Yellow	31.2 (35.4)	31.2 (36.5)	0.6 (4.2)	14.1 (16.2)	0.91
2-propanethiol +1,10-phenanthroline	60	864	$\text{C}_9\text{H}_{24}\text{S}_3\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Pink	30.6 (33.0)	32.2 (39.8)	4.6 (6.8)	14.0 (15.2)	0.83
2-methylpropane-2-thiol +1,10-phenanthroline	50	864	$\text{C}_{12}\text{H}_{27}\text{S}_3\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Yellow	21.8 (30.9)	39.6 (42.7)	4.7 (5.5)	13.7 (14.1)	0.97
Butanethiol +1,10-phenanthroline	40	864	$\text{C}_{12}\text{H}_{27}\text{S}_3\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Pink	29.1 (30.9)	40.1 (42.6)	4.6 (5.6)	12.6 (14.1)	0.89
1-pentanethiol +1,10-phenanthroline	40	864	$\text{C}_{15}\text{H}_{33}\text{S}_3\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Orange	26.3 (29.2)	40.7 (45.2)	4.8 (6.0)	11.2 (13.5)	0.94
Ethane-1, 2-dithiol +1,10-phenanthroline	50	864	$\text{C}_6\text{H}_{15}\text{S}_6\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Purple	29.0 (30.4)	28.3 (31.4)	0.3 (3.6)	25.6 (27.9)	0.88
Butane-1, 4-dithiol +1,10-phenanthroline	50	864	$\text{C}_{12}\text{H}_{27}\text{S}_6\text{Bi} \cdot \text{C}_{12}\text{H}_8\text{N}_2$	Purple	26.4 (27.1)	29.4 (39.3)	3.8 (4.7)	23.3 (24.9)	0.79

Table-III: Electrolysis Characteristics, Analytical and other Related Data of Electrolytic product of various thiol Systems + 2, 2' - bipyridyl at Bismuth Anode

System	Potential	Electricity Passed (Coulomb)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/ Faraday)
					Bi	C	H	S	
Ethanethiol + 2, 2' - bipyridyl	40	864	$\text{C}_6\text{H}_{15}\text{S}_3\text{Bi} \cdot \text{C}_{10}\text{H}_8\text{N}_2$	Dirty Yellow	37.5 (38.1)	31.0 (35.3)	3.9 (4.4)	15.3 (17.5)	0.92
2-propanethiol+ 2, 2' - bipyridyl	60	864	$\text{C}_9\text{H}_{24}\text{S}_3\text{Bi} \cdot \text{C}_{10}\text{H}_8\text{N}_2$	Yellow	36.4 (35.4)	30.4 (38.8)	2.6 (4.8)	14.8 (16.1)	0.81
2-methylpropane-2-thiol + 2, 2' - bipyridyl	50	864	$\text{C}_{12}\text{H}_{27}\text{S}_3\text{Bi} \cdot \text{C}_{10}\text{H}_8\text{N}_2$	Yellow	31.5 (33.0)	39.7 (41.7)	4.0 (5.6)	13.7 (15.1)	0.87
Butanethiol+ 2, 2' - bipyridyl	40	864	$\text{C}_{12}\text{H}_{27}\text{S}_3\text{Bi} \cdot \text{C}_{10}\text{H}_8\text{N}_2$	Orange	32.6 (33.0)	37.6 (41.7)	4.7 (5.6)	11.6 (15.1)	0.78
1-pentanethiol + 2, 2' - bipyridyl	40	864	$\text{C}_{15}\text{H}_{33}\text{NS}_3\text{Bi} \cdot \text{C}_{10}\text{H}_8\text{N}_2$	Orange	29.8 (31.3)	41.3 (44.7)	5.5 (6.1)	10.2 (14.5)	0.91
Ethane- 1, 2-dithiol+ 2, 2' -	50	864	$\text{C}_6\text{H}_{15}\text{S}_6\text{Bi} \cdot \text{C}_{10}\text{H}_8\text{N}_2$	Purple	30.6 (32.8)	26.3 (29.7)	2.8 (3.5)	27.6 (29.3)	0.81

bipyridyl									
Butane-1, 4-dithiol+ 2, 2' - bipyridyl	40	864	C ₁₂ H ₂₇ S ₆ B i. C ₁₀ H ₈ N ₂	Purple	26.6 (28.5)	15.6 (36.1)	0.6 (4.8)	21.3 (23.5)	0.84

Current efficiencies of some of these systems have also determined which are quite close to 100%, thereby indicating that the reactions leading to formation of coordination compounds are the predominant reactions of these systems.

IV. Conclusion

The project studies thus reveals that electrochemical method for synthesis of bismuth thiolates and their coordination compounds is a single step process and is quite simple as compared to other reported multistep methods for the synthesis of these compounds.

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