Direct Electrochemical Synthesis of Bismuth(III) Phenoxides and their Coordination Compounds

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Received 21 March 2011; Accepted 30 April 2011

ABSTRACT: Bismuth(III) phenoxides have been synthesized by electrochemical reactions of 1-naphthol, 2-naphthol, 4-aminophenol, 2-nitrophenol, 4-nitrophenol, 2-hydroxybenzoic acid, *p*-cresol, phenol, resorcinol, 2-tert-butylphenol and 2-tert-butyl-4-methoxyphenol at sacrificial bismuth anode and inert platinum cathode using tetrabutylammonium chloride as supporting electrolyte. The coordination compounds of these phenols with 1, 10-phenanthroline and 2, 2'-bipyridyl have also been synthesized electrochemically. The solid products 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: Electrochemical synthesis, Sacrificial electrode, *H*-type cell, Tetrabutylammonium chloride, Current efficiencies

Introduction

Electrochemical technique has widely been used in synthetic organic¹⁻⁵ and inorganic chemistry⁶⁻¹⁰. This technique is the direct route to carry out oxidation or reduction without introducing any foreign oxidizing or reducing agent. The most important advantages of this technique are the simplicity and high product yield. In continuation to our interest in the electrochemical synthesis of inorganic compounds¹¹⁻¹³, we report in this communication the synthesis of bismuth phenoxides and their coordination compounds.

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.

A *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 guage ($2.0 \times 1.0 \times 1.0 \text{ cm}^3$) was used as cathode and bismuth rod ($2.0 \times 10.0 \times 0.2 \text{ cm}^3$) 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 g of Phenols, 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 guage 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.

Bu_4NCl 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 earlier¹¹⁻¹³. 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 $4000\text{--}450 \text{ cm}^{-1}$ 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 method¹⁴. The microanalyses of C, H and N of these compounds have also been carried out.

Results and Discussion

The products obtained 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 up to 300°C , however, colour of these compounds changes around 230°C thereby indicating that these products decompose around this temperature.

The analytical data (bismuth, carbon, hydrogen and nitrogen contents in all these products) along with their electrolytic characteristics of these systems are summarized in Table 1. Perusal of Table 1 reveals that the analytical data conform to the molecular formula $\text{Bi}(\text{OPhX})_3$ where X is NH_2 , NO_2 , 2-tertbutyl and 2-tertbutyl-4-methoxy groups in various phenols except in case of 2-hydroxybenzoic acid where X denotes OH group.

Infrared spectra of all the electrochemical products (except that of 2-hydroxybenzoic acid) show no absorption band in the region of $3600\text{--}3400 \text{ cm}^{-1}$ thereby showing that the proton of phenolic group¹⁵ in these reactions has been replaced by anodic bismuth. All the products show absorption bands in the region of $680\text{--}670 \text{ cm}^{-1}$. Literature reveals¹⁵⁻¹⁷ that

the $\nu(\text{M-O})$ stretching bands appear in the region of $700\text{--}500\text{ cm}^{-1}$. Thus these bands appearing in the region of $680\text{--}670\text{ cm}^{-1}$ can be assigned to $\nu(\text{Bi-O})$ stretching vibrations¹⁸⁻¹⁹. Survey of literature reveals²⁰ that in metal aryloxides two types of bands due to $\nu(\text{C-O})$ M appear in the region of $1180\text{--}1010\text{ cm}^{-1}$. In the present products two types of bands appear in the region of $1158\text{--}1030\text{ cm}^{-1}$ due to $\nu(\text{C-O})$ Bi stretching vibrations. Bands in the region of $1158\text{--}1060\text{ cm}^{-1}$ may be assigned to terminal $\nu(\text{C-O})$ Bi phenoxy groups and the bands in the region of $1060\text{--}1030\text{ cm}^{-1}$ may be attributes to bridged $\nu(\text{C-O})$ Bi phenoxy groups.

Table 1. Electrolysis characteristics, analytical and other related data of electrolysis of phenols at bismuth anode

System	Potential	Electricity Passed (Coulombs)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/Faraday)
					Bi	C	H	N	
Phenol	50	864	$\text{C}_{18}\text{H}_{15}\text{O}_3\text{Bi}$	Cream	42.1	41.7	2.26	-	0.81
					42.8	44.2	3.07	-	
1-Naphthol	50	864	$\text{C}_{30}\text{H}_{21}\text{O}_3\text{Bi}$	Dark brown	31.8	56.0	4.52	-	0.76
					32.7	56.4	3.29	-	
2-Naphthol	50	864	$\text{C}_{30}\text{H}_{21}\text{O}_3\text{Bi}$	Dark brown	32.0	57.0	3.02	-	0.82
					32.7	56.4	3.29	-	
4-Aminophenol	50	864	$\text{C}_{18}\text{H}_{18}\text{N}_3\text{O}_3\text{Bi}$	Brown	39.0	40.1	3.01	6.5	0.90
					39.2	40.5	3.37	7.8	
2-Nitrophenol	50	864	$\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_9\text{Bi}$	Brown	33.2	33.1	1.5	6.3	0.92
					33.5	34.6	1.9	6.9	
4-Nitrophenol	50	864	$\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_9\text{Bi}$	Brown	32.1	33.2	1.1	5.9	0.91
					33.5	34.6	1.9	6.7	
<i>p</i> -Cresol	50	864	$\text{C}_{21}\text{H}_{21}\text{O}_3\text{Bi}$	Dirty white	38.3	45.1	3.6	-	0.77
					39.4	47.5	3.9	-	
Resorcinol	50	864	$\text{C}_{18}\text{H}_{15}\text{O}_6\text{Bi}$	Brown	36.5	40.0	1.1	-	0.79
					38.9	40.3	1.7	-	
2-tert-Butylphenol	50	864	$\text{C}_{30}\text{H}_{39}\text{O}_3\text{Bi}$	Dirty white	30.2	53.6	5.9	-	0.87
					31.8	54.8	5.9	-	
2-tert-Butyl-4-methoxyphenol	50	864	$\text{C}_{33}\text{H}_{45}\text{O}_6\text{Bi}$	Dirty white	27.2	52.6	6.0	-	0.82
					27.9	52.8	6.4	-	

Presence of bands due to bridged phenoxy groups in the infrared spectra of the products indicates their polymeric nature. Polymeric nature of the products is also supported by their high melting point and insoluble behaviour in various organic solvents.

The infrared spectral data of the electrochemical product of 2-hydroxybenzoic acid show characteristic bands at 3575 cm^{-1} , 1653 cm^{-1} and 1315 cm^{-1} . The band at 3575 cm^{-1} indicates that hydroxyl proton of 2-hydroxybenzoic acid is not replaced by anodic bismuth. Literature also reveals²¹ that carboxylate groups show characteristic absorption bands in the region of $1647\text{--}1636\text{ cm}^{-1}$, $1318\text{--}1308\text{ cm}^{-1}$ corresponding to asymmetric and symmetric stretching vibrations. The presence of bands at 1653 cm^{-1} and 1315 cm^{-1} in the present product thus can be assigned to asymmetric and symmetric stretching vibrations. Since the carboxylic group is more acidic than phenolic group, thus the proton of carboxylic group is replaced by anodic bismuth and phenolic group remains unaffected. In this product bands also appear at 1178 cm^{-1} , 1140 cm^{-1} , 1058 cm^{-1} and 677 cm^{-1} which can be assigned to bridged $\nu(\text{Bi-OH})$ ²², terminal $\nu(\text{C-O})$ Bi, bridged $\nu(\text{C-O})$ Bi and $\nu(\text{Bi-O})$ mode¹⁸⁻¹⁹ respectively.

Current efficiencies of these systems were also determined and are enlisted in Table 1. Perusal of Table 1 reveals that current efficiencies of various phenols at sacrificial bismuth anode are quite high. High current efficiencies of these systems indicate that the reactions leading to the formation of bismuth(III) phenoxides are the predominant reactions of these systems. The reaction scheme may be written as:

At inert cathode:

At sacrificial bismuth anode:

In case of 2-hydroxybenzoic acid, since the carboxylic group is easily reducible than phenolic group so reaction scheme may be written as:

At inert cathode:

At sacrificial bismuth anode:

Synthesis of coordination compounds

Electrochemically prepared bismuth(III) phenoxides have been refluxed with the ligand (1,10-phenanthroline or 2,2'-bipyridyl) in various solvents for 48 h in order to prepare coordination compounds of these phenoxides. Analytical data and infrared spectral data of these products show that no coordination products have been formed. It was, therefore, considered worthwhile that the ligand may be added to these phenoxides before these form phenoxy bridges. Therefore, in addition to the phenols and supporting electrolyte, 1.0 g of the ligand was also added to these systems and the solution was then electrolysed at bismuth anode.

The solid product separated in anode compartment was filtered, washed with dry ether and dried under vacuum. The analytical data (bismuth, carbon, hydrogen and nitrogen contents in all these products) along with there electrolytic characteristics of these systems are summarized in Table 2 and Table 3. The data conform to molecular formula $\text{Bi}(\text{OPhX})_3$ L.

The products obtained are insoluble in commonly used organic solvents. Melting point of all these products has also been determined. All these compounds do not melt up to 300 °C, however, colour of these compounds changes around 230 °C thereby indicating that these products decompose around this temperature.

Table 2. Electrolysis characteristics, analytical and other related data of electrolytic product of various phenol 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	N	
Phenol + 1, 10-phenanthroline	50	864	C ₃₀ H ₂₅ N ₂ O ₄ Bi	Brown	29.1 30.5	51.7 52.5	3.2 3.6	3.5 4.1	0.81
1-Naphthol + 1, 10-phenanthroline	50	864	C ₄₂ H ₃₁ N ₂ O ₄ Bi	Dark brown	24.3 24.9	59.8 60.3	2.7 3.7	3.0 3.3	0.86
2-Naphthol + 1, 10-phenanthroline	50	864	C ₄₂ H ₃₁ N ₂ O ₄ Bi	Brown	24.1 24.9	60.0 60.3	3.2 3.7	2.8 3.3	0.88
4-Aminophenol + 1,10-phenanthroline	50	864	C ₃₀ H ₂₈ N ₅ O ₄ Bi	Cream	27.3 28.6	46.1 49.2	3.0 3.8	9.5 9.6	0.89
2-Nitrophenol + 1,10-phenanthroline	50	864	C ₃₀ H ₂₂ N ₅ O ₁₀ Bi	Brown	25.2 25.4	40.1 43.8	2.5 2.6	8.3 8.5	0.92
4-Nitrophenol + 1,10-phenanthroline	50	864	C ₃₀ H ₂₂ N ₅ O ₁₀ Bi	Brown	24.9 25.4	42.6 43.8	1.9 2.6	8.6 8.5	0.91
<i>p</i> -Cresol + 1, 10-phenanthroline	50	864	C ₃₃ H ₃₁ N ₂ O ₄ Bi	Cream	28.3 28.7	54.1 54.4	3.6 4.2	3.3 3.9	0.71
Resorcinol + 1, 10-phenanthroline	50	864	C ₃₀ H ₂₈ N ₂ O ₇ Bi	Brown	27.5 28.5	45.0 49.0	2.0 3.8	3.7 3.8	0.72
2-tert-Butylphenol + 1,10-phenanthroline	50	864	C ₄₂ H ₄₉ N ₂ O ₄ Bi	Dark brown	24.2 24.5	55.6 59.0	5.9 5.7	3.1 3.3	0.87
2-tert-Butyl-4-methoxyphenol + 1,10-phenanthroline	50	864	C ₄₅ H ₃₈ N ₂ O ₇ Bi	Dark brown	22.2 22.1	55.6 57.0	5.9 6.1	2.2 2.9	0.88
2-Hydroxybenzoic acid + 1, 10-phenanthroline	50	864	C ₃₃ H ₂₅ N ₂ O ₁₀ Bi	Brown	27.2 27.1	51.6 51.4	2.9 3.2	2.9 3.6	0.72

Infrared spectral data of these products (except that of 2-hydroxybenzoic acid) show no absorption band corresponding to phenolic group¹⁵. Examination of infrared data of the products reveals that the characteristic bands appear in the regions of 690-680 cm⁻¹, 1070-1035 cm⁻¹, 1070-1165 cm⁻¹ and 1605-1585 cm⁻¹. The bands in the region of 690-680 cm⁻¹, 1070-1035 cm⁻¹ and 1070-1165 cm⁻¹, may be assigned to $\nu(\text{Bi-O})$ ¹⁸⁻¹⁹, $\nu(\text{C-O})$ Bi bridged and $\nu(\text{C-O})$ Bi terminal stretching mode²⁰ respectively. All these bands, however, appear in slightly higher region as compared to those in the parent phenoxides.

The additional bands observed in the infrared spectra of these products in the region of 1605-1585 cm⁻¹ are due to the ligand molecules and can be assigned to $\nu(\text{C-N})$ and $\nu(\text{C-C})$ stretching vibrations²². These bands also appear at slightly higher region as compared to those in the parent ligand molecules.

In case of coordination products of 2-hydroxybenzoic acid infrared data show absorption band in the region of 3360-3350 cm⁻¹ corresponding to phenolic group²³ and characteristic absorption bands due to carboxylate group in the region of 1642-1641 cm⁻¹ and 1315-1307 cm⁻¹ correspond to asymmetric and symmetric stretching vibrations respectively. In these products, bands also appear in the region of 690-680 cm⁻¹ due to

$\nu(\text{Bi-O})^{18-19}$, 1075-1048 cm^{-1} due to bridged $\nu(\text{C-O})$ Bi, 1075-1178 cm^{-1} correspond to terminal $\nu(\text{C-O})$ Bi, 1183-1182 cm^{-1} due to bridged $\nu(\text{Bi-OH})^{22}$ and 1605-1595 cm^{-1} due to $\nu(\text{C-N})$ and $\nu(\text{C-C})$ stretching vibrations respectively.

Table 3. Electrolysis characteristics, analytical and other related data of electrolytic product of various phenol 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	N	
Phenol + 2, 2' - bipyridyl	50	864	$\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_3\text{Bi}$	Brown	32.1 32.4	51.7 52.1	3.2 3.5	4.1 4.4	0.81
1-Naphthol + 2, 2' - bipyridyl	50	864	$\text{C}_{40}\text{H}_{29}\text{N}_2\text{O}_3\text{Bi}$	Brown	26.8 26.3	59.0 60.4	3.5 3.6	3.4 3.5	0.79
2-Naphthol + 2, 2' - bipyridyl	50	864	$\text{C}_{40}\text{H}_{29}\text{N}_2\text{O}_3\text{Bi}$	Dark brown	26.0 26.3	58.9 60.4	3.0 3.6	2.9 3.5	0.82
4-Aminophenol + 2, 2' - bipyridyl	50	864	$\text{C}_{28}\text{H}_{26}\text{N}_5\text{O}_3\text{Bi}$	Cream	30.0 30.3	46.1 48.8	3.0 3.7	9.5 10.2	0.91
2-Nitrophenol + 2, 2' - bipyridyl	50	864	$\text{C}_{28}\text{H}_{20}\text{N}_5\text{O}_9\text{Bi}$	Brown	25.2 26.8	41.1 43.1	1.5 2.5	8.3 8.9	0.82
4-Nitrophenol + 2, 2' - bipyridyl	50	864	$\text{C}_{28}\text{H}_{20}\text{N}_5\text{O}_9\text{Bi}$	Cream	26.1 26.8	43.2 43.1	2.1 2.5	7.9 8.9	0.86
<i>p</i> -Cresol + 2, 2' - bipyridyl	50	864	$\text{C}_{31}\text{H}_{29}\text{N}_2\text{O}_3\text{Bi}$	Brown	30.3 30.5	52.1 54.2	4.0 4.2	4.2 4.1	0.71
Resorcinol + 2, 2' - bipyridyl	50	864	$\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_6\text{Bi}$	Brown	30.0 30.2	47.9 48.5	2.9 3.3	4.1 4.0	0.72
2-tert-Butylphenol + 2, 2' - bipyridyl	50	864	$\text{C}_{40}\text{H}_{47}\text{N}_2\text{O}_3\text{Bi}$	Brown	24.9 25.7	55.6 59.1	5.9 5.7	2.8 3.5	0.90
2-tert-Butyl-4-methoxyphenol + 2, 2' - bipyridyl	50	864	$\text{C}_{43}\text{H}_{56}\text{N}_2\text{O}_6\text{Bi}$	Dark brown	23.2 23.1	57.6 57.0	6.9 6.1	3.2 3.1	0.88
2-Hydroxybenzoic acid + 2, 2' - bipyridyl	50	864	$\text{C}_{31}\text{H}_{23}\text{N}_2\text{O}_9\text{Bi}$	Dark brown	27.2 28.6	51.6 51.1	3.4 3.1	3.7 3.9	0.82

Shift of the $\nu(\text{Bi-O})$ and $\nu(\text{C-O})$ Bi, bands towards higher region and presence of $\nu(\text{C-N})$ and $\nu(\text{C-C})$ bands confirm the coordination of ligand to bismuth(III) phenolates. Appearance of bands due to terminal phenoxy groups, bridged phenoxy groups, insoluble behaviour in various organic solvents and high melting point indicates that these coordination compounds are also polymeric in nature.

Current efficiencies of all these reactions have been determined and the data are listed in Table 2 and Table 3. Perusal of Table 2 and Table 3 reveals that the current efficiencies of these systems are quite high thereby showing that the reactions leading to the formation of the coordination compounds of bismuth(III) phenolates are the predominant reactions of these systems. The reaction scheme can be given as:

At inert cathode:

At sacrificial bismuth anode:

The reaction scheme for the 2-hydroxybenzoic acid + ligand system may be written as:

At inert cathode:

At sacrificial bismuth anode:

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