

Synthesis of Antimony(III) Phenolates and their Coordination Compounds

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Reactions of phenol, 4-aminophenol, 4-nitrophenol, 2-nitrophenol, 2,4-dinitrophenol, 2-tert-butylphenol and 2-tert-butylphenol in acetonitrile at sacrificial antimony anode using tetrabutylammonium chloride. The products formed analyzed by infrared spectral studies and are identified to be antimony(III) phenolates. Coordination compounds of all these antimony(III) phenolates also been synthesized.

Keywords: Antimony, Acetonitrile, Tetrabutylammonium chloride, 1,10-Phenanthroline, 2,2'-Bipyridyl.

INTRODUCTION

Present study deals with the reactions proceeding at the expense of external electrical energy. It has been used as a synthetic method in organic chemistry [1-8] for the last so many years. The first useful organosynthesis was made by Faraday [9] by electrolyzing potassium acetate solution followed by the electrolysis of salts of carboxylic acids (the anodic oxidation of which yields hydrocarbons) was generalized by Kolbe [10] in 1847. The use of this technique in organic synthesis was later extended by Brown and Walker [11,12]. These were followed by the development of a number of reactions [13] such as coupling reactions [8,14,15], substitution reactions [16,17], electron transfer reactions [18], conversion reactions [18], polymerization reactions [19,20] and chiral induction reactions [21,22]. Some of these reactions were also used on industrial scale [23-26].

Antimony and its compounds play important role in our daily life. Antimony compounds have been employed medicinally [27] since ancient times. Trivalent organoantimony compounds have been used in a wide variety of reactions such as self-coupling reactions and cross-coupling reactions [28]. Optically active [29,30] organoantimony compounds are utilized for asymmetric synthesis, *i.e.*, synthesis of optically active antimony compounds. Organoantimony compounds also exhibit signifi-cant antimicrobial as well as antitumor activities which are associated with cytostatic activities [31].

In view of the fact that the electrochemical methods provide unique path of a large variety of chemical compounds and the technique is associated with several advantages over the conventional synthetic methods. Antimony is chosen for present studies as its compounds play important role in our daily life, medicines and industry.

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Present work, therefore, presents the electrochemical reactions of different types of organic compounds at sacrificial antimony electrode. The products of these reactions are isolated and characterized.Survey of literature revealed [32] that this technique is associated with several advantages over the conventional synthetic methods. In the light of above advantages here the author presents electrochemical synthesis and characterization of antimony(III) phenolates and their coordination compounds.

EXPERIMENTAL

Electrolytic cell: Electrolysis was carried out in 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. Both compartments were provided with two openings; one for guard tube and the other for the electrode. Platinum foil $(1.0 \text{ cm} \times 1.0 \text{ cm})$ and antimony sheet $(2.0 \text{ cm} \times 10 \text{ cm} \times 0.2 \text{ cm})$ were used as cathode and anode respectively. The electrolytic solution in the anode compartment was stirred efficiently using magnetic stirrer.

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The direct current power supply was fitted with a voltmeter capable of indicating potential from 0-100 V and an ammeter capable of indicating 20-50 mA of the current.

All the reagents *viz.*, acetone, acetonitrile, diethyl ether were purified by standard method and tetrabutylammonium chloride used as supporting electrolyte.

Electrochemical reactions of phenols at antimony anode: Decomposition potential (the potential at which the substrate loses electrons at the anode surface) of phenol was determined, which was found to be less than 1.5 V. Electrochemical reactions of the solution of these alcohols in acetonitrile containing tetrabutylammonium chloride have been conducted at sacrificial antimony anode in a H-type cell at a potential corresponding to the decomposition potential of the alcohol for more than 48 h. After such prolonged electrolysis, no product separated in the anode compartment, however, the solution in the anode compartment turned slightly turbid. The solution from anode compartments was concentrated but no product could be isolated. This may be due to the following reasons:

(I) The current flowing through the solution at a potential of 1.5 V or even less than this is just a small fraction of a mill-ampere, as a result a very small amount of the product is formed.

(II) The solution contained a large amount of supporting electrolyte, thus it was very difficult to isolate the small amount of the product from such a reaction mixture.

Keeping this in view and to increase the rate of formation of products, the reaction conditions have been modified as the aim of the present studies is the synthesis of inorganic and organometallic compounds. The modified conditions are:

(I) Transport number determination of the electrolytes in various solvents by Hitroff's method.

(II) The concentration of the supporting electrolyte was sufficiently decreased as compared to the concentration required in methods like polarographic or other voltametric methods so that the products could be easily separated from the reaction mixture.

(III) The solution has been stirred thoroughly during the process of electrolysis. The stirring not only increases the rate of reaction but also helps in removing the products sticking to the electrode surface.

In the present studies the emphasis is to explore the use of the electrochemical technique as a synthetic tool, so isolation of pure products in a shorter time is the primary object of this study. Therefore, the electrochemical reactions of the organic compound (2.0 g), acetonitrile (250 mL) and supporting electrolyte *i.e.*, tetrabutylammonium chloride (1.0 g) was carried out. The electrolytic cell can be represented as:

$$Sb_{(+)} \begin{vmatrix} Phenol \\ +CH_3CN + Bu_4NCl \end{vmatrix} Pt_{(-)}$$

where: Sb(+) is antimony anode and Pt(-) is platinum cathode.

Electrolysis has been carried out. The solid products separated after electrolysis were filtered in a filtration unit of G-3 porosity. Products were then kept in desicator to avoid direct contact with air and moisture.

Ratio of antimony contents in products determined volumetrically. Microanalysis for carbon, hydrogen and nitrogen contents of these products has also been carried out.

RESULTS AND DISCUSSION

Synthesis of antimony(III) phenolates: The products of the these electrochemical reactions 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. The contents of antimony, carbon, nitrogen and hydrogen contents in all the products are summarized in Table-1, which confirm Sb(OPhX)₃ compounds.

Compounds formed has characteristic vibrations in the regions of 580-540, 1060-1000 and 1148-1060 cm⁻¹. Literature revealed [33] that v(Sb-O) vibrations appear in the region of 612-540 cm⁻¹. The vibrations from 580-540 cm⁻¹ in the these compounds can be assigned to v(Sb-O) vibrations.

Early studies [34] revealed that in alkoxides vibrations due to v(C-O)M appear in the region of 1160-1000 cm⁻¹, one medium intensity band from 1160-1060 cm⁻¹ appears due to terminal v(C-O)M vibrations and vibrations from 1060-1000 cm⁻¹ due to bridged v(C-O)M mode. In these compounds vibrations appears in 1148-1000 cm⁻¹. Vibrations in 1060-1000 cm⁻¹ and 1148-1060 cm⁻¹ can be assign to v(C-O)Sb bridge and terminal vibration respectively. Bridged vibrations in the infrared spectra indicates their polymeric nature.

The plausible structure may be given as:



At inert cathode:



At sacrificial antimony anode:



Synthesis of the coordination compounds of antimony(III) phenolates: Coordination compounds can be prepared by electrolyzing phenols and supporting electrolyte, 1.0 g of the ligand was also added to these systems and the solution was then electrolyzed at antimony sacrificial anode and inert platinum cathode. The electrolytic characteristics of all the system are summarized in Table-2.

The products formed are summarized in Table-2, which conform to the molecular formula, Sb(OPhX)₃·L.

The extra vibrations appear in coordination compounds than parent compounds observed from 1585-1605 cm⁻¹ are due

TABLE-1 ELECTROLYSIS CHARACTERISTICS, ANALYTICAL AND OTHER RELATED DATA OF ELECTROLYTIC PRODUCT OF PHENOL SYSTEMS AT ANTIMONY ANODE

Phenol	Potential applied (V)	Electricity passed (Coulombs)	Products	Colour	Eleme	Current efficiencies			
					Sb	С	Н	Ν	equivalent/ Faraday)
Phenol	30	720	$C_{18}H_{15}O_3Sb$	Dirty	30.43	53.79	2.29	-	0.96
				white	(30.38)	(53.89)	(3.74)		
2-Hydroxybenzoic	30	720	$C_{21}H_{15}O_9Sb$	Dirty	22.8	46.89	2.49	-	0.90
acid				white	(22.85)	(47.30)	(2.81)		
4-Aminophenol	30	720	$C_{18}H_{18}N_{3}O_{3}Sb$	Brown	27.39	48.23	3.79	8.43	0.80
					(27.31)	(48.45)	(4.03)	(9.42)	
4-Nitrophenol	30	720	$C_{18}H_{12}N_2O_9Sb$	Brown	21.10	40.84	2.69	7.02	0.97
-					(21.40)	(41.29)	(2.23)	(7.83)	
2-Nitrophenol	30	720	$C_{18}H_{12}N_2O_9Sb$	Light	18.20	40.56	1.98	5.28	0.83
-				brown	(18.48)	(41.39)	(2.29)	(5.36)	
2,4-Dinitrophenol	30	720	$C_{18}H_9N_6O_{15}Sb$	Brown	21.1	31.46	1.23	11.74	0.92
					(22.72)	(32.20)	(1.34)	(12.52)	
2-tert-Butylphenol	30	720	$C_{30}H_{39}O_{3}Sb$	Dirty	21.30	62.79	5.23	_	0.78
• 1			50 57 5	white	(22.72)	(63.29)	(6.85)		
2-tert-Butyl-4-	30	720	$C_{33}H_{45}O_6Sb$	Dirty	17.32	58.39	6.47	_	0.85
methoxyphenol			55 15 0	white	(18.15)	(60.11)	(6.83)		

TABLE-2 ELECTROLYSIS CHARACTERISTICS, ANALYTICAL AND OTHER RELATED DATA OF ELECTROLYTIC PRODUCT OF PHENOL + LIGAND SYSTEMS AT ANTIMONY ANODE

Phenol	Potential applied (V)	Electricity passed (Coulombs)	Products	Colour	Elemental analysis (%): Found (calcd.)				Current efficiencies (Gram-
					Sb	С	Н	Ν	equivalent/ Faraday)
Phenol +	50	720	$C_{18}H_{15}O_{3}SbC_{12}H_{8}N_{2} \\$	Dirty	19.7	60.54	2.87	3.23	0.74
1,10-phenanthroline				white	(20.8)	(61.98)	(3.96)	(4.82)	
2-Hydroxybenzoic acid + 1,10-phenanthroline	50	720	$C_{21}H_{15}O_9SbC_{12}H_8N_2$	Dirty white	16.7 (17.08)	52.48 (55.55)	2.47 (3.22)	3.41 (3.92)	0.97
4-Aminophenol + 1,10-phenanthroline	50	720	$C_{18}H_{18}N_3O_3SbC_{12}H_8N_2$	Dirty white	19.7 (19.4)	56.21 (57.53)	3.08 (4.15)	10.78 (11.18)	0.85
4-Nitrophenol + 1,10-phenanthroline	50	720	$C_{18}H_{12}N_2O_9SbC_{12}H_8N_2$	Light brown	16.7 (17.01)	48.56 (50.29)	2.45 (2.79)	8.45 (9.77)	0.79
2-Nitrophenol + 1,10-phenanthroline	50	720	$C_{18}H_{12}N_2O_9SbC_{12}H_8N_2$	Light brown	16.7 (17.01)	49.28 (50.29)	2.39 (2.79)	8.72 (9.77)	0.95
2,4-Dinitrophenol + 1,10-phenanthroline	50	720	$C_{18}H_9N_6O_{15}SbC_{12}H_8N_2$	Light brown	13.6 (14.23)	40.84 (42.31)	1.47 (1.99)	12.97 (13.16)	0.84
2- <i>tert</i> -Butylphenol + 1,10-phenanthroline	50	720	$C_{30}H_{39}O_{3}SbC_{12}H_{8}N_{2} \\$	Dirty white	16.7 (16.2)	67.25 (67.31)	5.38 (6.27)	3.47 (3.73)	0.91
2- <i>tert</i> -Butyl-4-methoyx- phenol +1,10phenanthroline	50	720	$C_{33}H_{45}O_6SbC_{12}H_8N_2$	Dirty white	13.6 (14.5)	63.72 (64.38)	6.87 (6.31)	2.56 (3.33)	0.76
Phenol + 2,2'-Bipyridyl	30	720	$C_{18}H_{15}O_{3}Sb\ C_{10}H_{8}N_{2}$	Light brown	21.1 (21.76)	58.47 (60.35)	3.86 (4.10)	4.34 (5.02)	0.97
2-Hydroxybenzoic acid + 2,2'-Bipyridyl	30	720	$C_{21}H_{15}O_9SbC_{10}H_8N_2$	Dirty white	18.26 (17.67)	53.24 54.01	3.84 (3.33)	4.53 (4.06)	0.85
4-Aminophenol + 2,2'-Bipyridyl	30	720	$C_{18}H_{18}N_3O_3SbC_{10}H_8N_2$	Light brown	19.75 (20.23)	55.42 (55.83)	4.15 (4.32)	10.19 (11.63)	0.91
4-Nitrophenol + 2,2'-Bipyridyl	30	720	$C_{18}H_{12}N_2O_9SbC_{10}H_8N_2$	Light brown	16.7 (17.6)	48.11 (48.57)	2.34 (2.89)	9.78 (10.11)	0.74
2-Nitrophenol + 2,2'-Bipyridyl	30	720	$C_{18}H_{12}N_2O_9SbC_{10}H_8N_2$	Light brown	18.26 (17.6)	47.59 (48.57)	2.47 (2.89)	9.54 (10.11)	0.87
2,4-Dinitrophenol + 2,2'-Bipyridyl	30	720	$C_{18}H_9N_6O_{15}SbC_{10}H_8N_2$	Light brown	13.65 (14.72)	38.98 (40.64)	1.87 (2.05)	12.34 (13.55)	0.76
2- <i>tert</i> -Butylphenol + 2,2'-Bipyridyl	30	720	$C_{30}H_{39}O_{3}SbC_{10}H_{8}N_{2} \\$	Dirty white	16.7 (16.79)	66.78 (66.22)	5.49 (6.48)	3.19 (3.86)	0.98
2- <i>tert</i> -Butyl-4-methoxy- phenol + 2,2'-Bipyridyl	30	720	$C_{33}H_{45}O_6SbC_{10}H_8N_2$	Dirty white	13.65 (14.9)	62.72 (63.33)	6.78 (6.50)	3.28 (3.43)	0.82

to the $v(C \rightarrow N)$ and $v(C \rightarrow C)$ vibrations [35] in the ligand molecule. The vibrations are in higher value.

The vibrations of the v(Sb-O) and v(C-O)Sb in upper region and presence of bands due to ligand molecules indicates ligand has been attached. Bridged vibrations, insoluble behaviour and high melting point indicate that these products are also polymeric in nature.

At inert cathode:



At sacrificial antimony anode:



The present studies provide a new route for the synthesis of antimony(III) phenoxides and their coordination compounds with 1,10-phenanthroline and 2,2'-bipyridyl. It is a single pot and direct synthetic method associated with high current efficiencies.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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