Electrochemical Synthesis of Organoantimony Compounds and their Coordination Compounds

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Electrochemical reactions of bromoethane, 1-bromopropane, 1-chlorobutane and chlorobenzene have been carried out in acetonitrile at sacrificial antimony anode using tetrabutylammonium chloride as supporting electrolyte. The products isolated from the anode compartment have been characterized by elemental analysis and infrared spectral studies and are identified as organoantimony compounds. Coordination compounds of same have been synthesized with ligand (1,10-phenanthroline and 2,2'-bipyridyl). All these reactions proceed with high current efficiencies.

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

INTRODUCTION

Due to adverse effects of antimony and its compounds on human life are considered to be priority pollutants interest by the USEPA and the EU, as it enters in environment in a significant amount through widely use in industries. Medicinally, trivalent organoantimony compounds have been used widely in a variety of reactions *viz.*, cross-coupling, self-coupling reactions, *etc*. Optically active organoantimony compounds are utilized for asymmetric synthesis, *i.e.*, synthesis of optically active antimony compounds. Antimony compounds also exhibit significant biological activity [1], catalytic oxidation [2], antimicrobial, antitumor activities [3], antileishmanial activity [4] as well as cytostatic activities [5].

A close study of suggests that the electrochemical synthetic technique has many advantages over the conventional synthetic methods such as: (a) It minimizes the number of chemicals employed as reactions are carried out without introducing any foreign oxidizing or reducing reagent into reaction mixture. The product thus can be easily isolated in comparatively pure form directly from the reaction mixture. (b) The electrochemical methods are extremely selective. In case the product can further undergo oxidation or reduction, the desired product can be obtained by the application of appropriate potential across the electrodes. (c) The yield of this method is invariably high as compared to other synthetic methods like thermal and photochemical methods. Generally, the electrochemical method gives quantitative yield of the desired product. (d) This method usually needs low-cost starting material as the reaction can directly be conducted with metal instead of using its costly compounds. (e) This technique does not cause any pollution problem, thus is a keen step towards green chemistry [6,7]. (f) The technique generally provides shortcut routes to multi-step reactions. (g) The rate of electrochemical reactions depends both on temperature and potential, whereas in case of chemical reactions, it depends only upon temperature. In this method by changing the potential one can change the reaction rate many times at the same temperature which otherwise is difficult to attain in chemical reactions [8,9]. Thus, electrochemical reactions can be conducted at ambient temperatures. (h) The electrochemical reactions have low activation energy and hence these are fast reactions as compared to usual chemical reactions.

EXPERIMENTAL

Electrolytic cell: Electrolysis was carried out in 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. Both compartments were provided with two openings; one for guard tube and the other for the electrode. Platinum foil (1.0 cm × 1.0 cm) and antimony sheet (2.0 cm × 10 cm × 0.2 cm) were used as cathode and anode

respectively. The electrolytic solution in the anode compartment was stirred efficiently using magnetic stirrer.

Estimation of antimony: Antimony contents in all these products were determined iodometrically: Accurately weighed amount of the product (200 mg) was heated to dryness four times with 5.0 mL of fuming nitric acid. The dry mass was then dissolved in water and 5 mL hydrochloric acid and then diluted to 100 mL in measuring flask (solution 'Z'). 20 mL of the solution 'Z' was taken in a glass-stoppered conical flask. 3 mL of the 4 M of hydrochloric acid was added to it. Air was displaced by introducing 0.4 g sodium hydrogen carbonate into the flask. The solution was then allowed to stand for at least 5 min after adding 1.0 g of pure potassium iodide to it. It was then titrated against 0.1 N sodium thiosulphate solution.

Determination of current efficiency: The current efficiencies (gram equivalents of antimony dissolved per faraday) of all these systems were determined by conducting the electrolysis of above systems under similar conditions but at constant current of 20 mA for exact 2 h. The solution from anode compartment was taken out. The anode compartment of the cell and anode was washed three times with acetonitrile. The solution of the anode compartment along with its washings was distilled in film evaporator until about 10 mL of contents were left in the flask. The contents were then transferred to a beaker and heated to dryness. Antimony contents were then determined in the dry mass as discussed above. The ratio of experimental and theoretical antimony contents gives the current efficiency of the system.

Calculations:

Experimental amount of Antimony found = C %

$$\text{Quantity of electricity passed} = \frac{2 \times 60 \times 60 \times 20}{1000} \text{ coulombs}$$

$$= 144 \text{ coulombs}$$

Theoretical amount of antimony dissolved by passing above quantity of electricity $= \dfrac{144 \times 121.75}{96487 \times 3}$ g

$$= 0.06057 \text{ g (say)}$$

$$\text{Current efficiency} = \frac{C}{0.06057} \text{ g-eq faraday}^{-1}$$

RESULTS AND DISCUSSION

Electrochemical reactions of alkyl halides/aryl halide at antimony anode: Electrolysis of bromoethane, 1-bromo-propane, 1-chlorobutane and chlorobenzene in the following electrolytic cell at antimony anode yields solid products. The cell can be represented as:

$$Sb_{(+)} \left| \begin{array}{c} RX/Ar\text{-}X + Bu_4NCl + \\ CH_3CN \end{array} \right| Pt_{(-)}$$
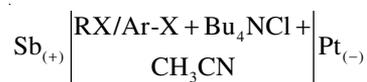
where: $Sb_{(+)}$ is antimony anode; $Pt_{(-)}$ is platinum cathode; Bu_4NCl is the supporting electrolyte; RX/Ar-X is alkyl halide/aryl halide used in the systems.

These products are quite stable and are not much affected by air and moisture. All these products are insoluble in various organic solvents, therefore, their molecular weight could not be determined. Melting point measurements of these products reveal that the products change their colour in the temperature range of 200 to 250 °C and do not melt up to 300 °C. Antimony, carbon, hydrogen and halogen contents in the products have also been determined and the relevant analytical data are summarized in Table-1. The data in Table-1 confirmed the molecular formula, $(R)_2SbX$.

Infrared spectra of the products have been recorded using potassium bromide pellets in the region of 4000-100 cm^{-1} and the relevant key bands are summarized in Table-2. The characteristic bands appear in the regions of 472-463 cm^{-1} and 168-156 cm^{-1}. Literature revealed [10,11] that ν(Sb–C) absorption bands appear in the region of 484-459 cm^{-1}. Thus the bands appearing in the region of 472-463 cm^{-1} in the present products can be assigned to ν(Sb–C) stretching vibrations. It is also reported in literature [12] that absorption bands due to (Sb-X) appear in the region of 200-156 cm^{-1}. Therefore, presence of the bands in the region of 168-156 cm^{-1} in the infrared spectrum of the present products can be assigned to ν(Sb–X) stretching vibrations.

TABLE-2
SELECTED INFRARED ABSORPTION BANDS
OF PRODUCTS OF ELECTROLYSIS OF ALKYL
HALIDES/CHLOROBENZENE AT ANTIMONY ANODE

System	Absorption bands (cm^{-1})	Possible assignment
Bromoethane	468 (s)	ν(Sb–C)
	461(s)	ν(Sb–Br)
1-Bromopropane	463 (s)	ν(Sb–C)
	458 (s)	ν(Sb–Br)
1-Chlorobutane	472 (s)	ν(Sb–C)
	452 (s)	ν(Sb–Cl)
Chlorobenzene	470 (s)	ν(Sb–C)
	461 (s)	ν(Sb-Cl)

TABLE-1
ELECTROLYSIS CHARACTERISTICS, ANALYTICAL AND OTHER RELATED DATA OF ELECTROLYTIC
PRODUCTS OF ALKYL HALIDES/CHLOROBENZENE SYSTEMS AT ANTIMONY ANODE

System	Potential applied (V)	Electricity passed (Coulombs)	Product	Colour	Elemental analysis (%): Found (calcd.)				Current efficiencies (Gram-equivalent/ Faraday
					Sb	C	H	Br/Cl	
Bromoethane	30	720	$(C_2H_5)_2SbBr$	Light brown	46.72 (46.88)	17.83 (18.48)	3.78 (3.85)	30.42 (30.77)	1.86
1-Bromopropane	40	720	$(C_3H_7)_2SbBr$	Light brown	42.24 (42.32)	24.54 (25.03)	4.16 (4.86)	27.34 (27.77)	1.45
1-Chlorobutane	50	720	$(C_4H_9)_2SbCl$	Light brown	44.36 (44.87)	34.85 (35.41)	6.47 (6.63)	12.96 (13.06)	0.97
Chlorobenzene	30	720	$(C_6H_5)_2SbCl$	Light brown	38.42 (39.10)	45.86 (46.29)	2.76 (3.21)	11.27 (11.38)	0.84

Current efficiencies of all these systems have been determined and its value are given in Table-3. It is revealed that the current efficiencies of all these systems are unusually high, *i.e.* more than one. High current efficiencies of all these systems can be explained on the basis the following reaction mechanism.

TABLE-3
CURRENT EFFICIENCIES OF ELECTROCHEMICAL REACTIONS ALKYL HALIDES/CHLOROBENZENE AT DIFFERENT INTERVALS OF TIME

System	Time (h)	Current efficiency (Gram equivalent/Faraday)
Bromoethane	0.5	2.85
	1.0	2.15
	2.0	1.86
	3.0	0.87
1-Bromopropane	0.5	2.65
	1.0	1.74
	2.0	1.45
	3.0	0.71
1-Chlorobutane	0.5	2.15
	1.0	1.49
	2.0	0.97
	3.0	0.67
Chlorobenzene	0.5	1.57
	1.0	1.23
	2.0	0.84
	3.0	0.64

At inert cathode:

$$RX + e^- \longrightarrow \dot{R} + X^- \tag{1}$$

The halide ions formed at cathode migrate to the anode compartment under the influence of applied potential and undergo the following sequence of reactions:

At sacrificial anode:

$$X^- \longrightarrow \dot{X} + e^- \tag{2}$$

$$\dot{X} + Sb_{(+)} \longrightarrow Sb\dot{X} \tag{3}$$

$$Sb\dot{X} + 2RX \longrightarrow (R)_2 SbX + 2\dot{X} \tag{4}$$
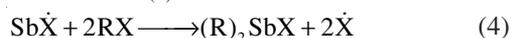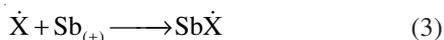
The reactions (3) and (4) constitute a chain process and proceed without the consumption of any current from the source and thus explain the high current efficiencies of these systems.

Coordination compounds of organoantimony compounds: Electrochemical reactions of the solutions containing alkyl/aryl halides, ligand and supporting electrolyte have been conducted at antimony anode and inert platinum cathode for 10 h in H-type cell.

The cell may be represented as:

$$Sb_{(+)} \left| \begin{array}{c} RX + Bu_4NCl + CH_3CN \\ + L \end{array} \right| Pt_{(-)}$$
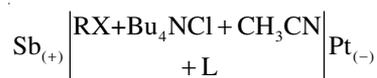
(The symbols have their usual meanings) L is ligand 1,10-phenanthroline and 2,2'-bipyridyl.

The products separated in the anode compartment are isolated. The products obtained are insoluble in commonly used organic solvents. Due to insoluble behavior, the molecular weight of these compounds could not be determined. The products are stable upto 300 °C, however, colour of these products changes between a temperature range of 230 to 250 °C thereby indicating that these products decompose around this temperature. Antimony contents in all these products were determined iodometrically. Analytical data are given in Table-4 and confirmed the molecular formula, $(R)_2SbX.L$.

Infrared spectra of the products have been recorded on Perkin-Elmer spectrophotometer (RXI) in the region of 4000-100 cm^{-1} using potassium bromide pellets and the key absorption bands are listed in Table-5.

Infrared spectral data reveal that characteristic bands appear in the regions of 484-468, 465-457 and 1605-1587 cm^{-1}. The bands appearing in the regions of 484-468 and 465-457 cm^{-1} in the present products can be assigned to ν(Sb-C) [10,11] and ν(Sb-X) [12] stretching vibrations respectively. Comparison of the present infrared data to those of the parent products shows a shift of these bands towards the higher regions. The additional bands appearing in the region of 1545-1455 cm^{-1} in these products may be due to ν(C⋯C) and ν(C⋯N) stret-

TABLE-4
ELECTROLYSIS CHARACTERISTICS, ANALYTICAL AND OTHER RELATED DATA OF ELECTROLYTIC PRODUCTS OF ALKYL HALIDES/CHLOROBENZENE + LIGAND SYSTEMS AT ANTIMONY ANODE

System	Potential applied (V)	Electricity passed (Coulombs)	Product	Colour	Elemental analysis (%): Found (calcd.)				Current efficiencies (Gram-equivalent/Faraday
					Sb	C	H	Br/Cl	
Bromoethane + 1,10-phenanthroline	40	720	$(C_2H_5)_2SbBrC_{12}H_8N_2$	Light brown	27.32 (27.68)	43.28 (43.69)	3.87 (4.09)	17.49 (18.16)	0.94
1-Bromopropane + 1,10-phenanthroline	50	720	$(C_3H_7)_2SbBrC_{12}H_8N_2$	Light brown	25.29 (26.03)	45.92 (46.21)	4.17 (4.70)	17.43 (17.07)	0.84
1-Chlorobutane + 1,10-phenanthroline	30	720	$(C_4H_9)_2SbClC_{12}H_8N_2$	Light brown	26.43 (26.97)	53.19 (53.21)	5.48 (5.75)	7.46 (7.85)	0.91
Chlorobenzene + 1,10-phenanthroline	30	720	$(C_6H_5)_2SbClC_{12}H_8N_2$	Light brown	24.45 (24.77)	58.64 (58.65)	3.24 (3.66)	7.09 (7.21)	0.97
Bromoethane + 2,2'-Bipyridyl	30	720	$(C_2H_5)_2SbBrC_{10}H_8N_2$	Light brown	28.92 (29.28)	40.18 (40.44)	4.27 (4.32)	19.17 (19.21)	0.97
1-Bromopropane + 2,2'-Bipyridyl	50	720	$(C_3H_7)_2SbBrC_{10}H_8N_2$	Light brown	26.85 (27.43)	43.11 (43.29)	4.26 (4.95)	17.54 (18.00)	0.94
1-Chlorobutane + 2,2'-Bipyridyl	30	720	$(C_4H_9)_2SbClC_{10}H_8N_2$	Light brown	28.34 (28.48)	50.27 (50.58)	5.29 (6.08)	8.25 (8.29)	0.91
Chlorobenzene + 2,2'-Bipyridyl	40	720	$(C_6H_5)_2SbClC_{10}H_8N_2$	Light brown	25.42 (26.04)	55.91 (56.52)	4.23 (4.27)	7.23 (7.58)	0.93

TABLE-5
SELECTED INFRARED ABSORPTION BANDS OF PRODUCTS
OF ELECTROLYSIS OF ALKYL HALIDES/CHLOROBENZENE
+ LIGAND SYSTEMS AT ANTIMONY ANODE

Systems	Absorption bands (cm^{-1})	Possible assignment
Bromoethane + 1,10-phenanthroline	484 (s)	ν(Sb–C)
	465 (s)	ν(Sb–Br)
	1602 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
1-Bromopropane + 1,10-phenanthroline	468 (s)	ν(Sb–C)
	461 (s)	ν(Sb–Br)
	1587 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
1-Chlorobutane + 1,10-phenanthroline	482 (s)	(Sb–C)
	465 (s)	ν(Sb–Cl)
	1605 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
Chlorobenzene + 1,10-phenanthroline	484 (s)	ν(Sb–C)
	457 (s)	ν(Sb–Cl)
	1601 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
Bromoethane + 2,2'-Bipyridyl	472 (s)	ν(Sb–C)
	460 (s)	ν(Sb–Br)
	1592 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
1-Bromopropane + 2,2'-Bipyridyl	472 (s)	ν(Sb–C)
	462 (s)	ν(Sb–Br)
	1604 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
1-Chlorobutane + 2,2'-Bipyridyl	468 (s)	ν(Sb–C)
	465 (s)	ν(Sb–Cl)
	1593 (s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$
Chlorobenzene + 2,2'-Bipyridyl	472(s)	ν(Sb–C)
	457(s)	ν(Sb–Cl)
	1598(s)	$\begin{bmatrix} \nu(C\!=\!=\!=\!N) \\ \nu(C\!=\!=\!=\!C) \end{bmatrix}$

TABLE-6
CURRENT EFFICIENCIES OF ELECTROCHEMICAL
REACTIONS OF ALKYL HALIDES/CHLOROBENZENE +
LIGAND AT DIFFERENT INTERVALS OF TIME

System	Time (h)	Current efficiency (Gram equivalent/Faraday)
Bromoethane + 1,10-phenanthroline	0.5	2.98
	1.0	1.32
	2.0	0.94
	3.0	0.64
1-Bromopropane + 1,10-phenanthroline	0.5	2.47
	1.0	1.74
	2.0	0.84
	3.0	0.78
1-Chlorobutane + 1,10-phenanthroline	0.5	2.65
	1.0	1.46
	2.0	0.91
	3.0	0.68
Chlorobenzene + 1,10-phenanthroline	0.5	2.19
	1.0	1.26
	2.0	0.97
	3.0	0.78
Bromoethane + 2,2'-Bipyridyl	0.5	2.18
	1.0	1.36
	2.0	0.97
	3.0	0.71
1-Bromopropane + 2,2'-Bipyridyl	0.5	2.36
	1.0	1.42
	2.0	0.94
	3.0	0.76
1-Chlorobutane + 2,2'-Bipyridyl	0.5	2.43
	1.0	1.26
	2.0	0.91
	3.0	0.77
Chlorobenzene + 2,2'-Bipyridyl	0.5	2.4
	1.0	1.26
	2.0	0.93
	3.0	0.78

$$\dot{X} + Sb_{(+)} \longrightarrow Sb\dot{X} \qquad (7)$$

$$Sb\dot{X} + 2RX + L \longrightarrow (R)_2SbX.L + 2\dot{X} \qquad (8)$$
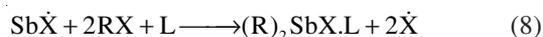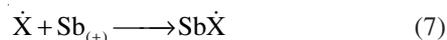
The reactions (7) and (8) constitute a chain process and proceed without the consumption of any current from the source and thus explain the quite high current efficiencies.

CONFLICT OF INTEREST

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

ching vibrations of the ligand molecules. However, these bands appear at slightly higher region as compared to those reported in the pure ligand molecules [13]. The shift of ν(Sb-C) and ν(Sb-X) bands towards higher region than those of the parent organoantimony compounds and presence of bands due to ligand molecules in the region of 1545-1455 cm^{-1} conform the coordination of the ligand.

Current efficiencies of all these systems are found to be very high (Table-6). High current efficiencies indicate that the reactions leading to the formation of coordination compounds of organoantimony are the predominant reactions of the systems. The reaction scheme is given below:

At inert cathode:

$$RX + e^- \longrightarrow \dot{R} + X^- \qquad (5)$$

The halide ions formed at cathode migrate to the anode compartment under the influence of applied potential and undergo there following sequence of reactions:

At sacrificial anode:

$$X^- \longrightarrow \dot{X} + e^- \qquad (6)$$

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