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Electrochemical Synthesis of Coordination Compounds of Antimony(III) Thiolates

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Abstract:
The antimony(III) thiolate, synthesized, have been refluxed with 1,10 - phenanthroline and 2,2’ - bipyridyl separately in various solvents like methanol, ethanol, benzene and acetonitrile for 48 hours in order to prepare their coordination compounds. Analytical data and infrared spectral data of the products so obtained show that the ligand molecules could not enter the coordination sphere of these antimony(III) thiolate. It is, therefore, considered worthwhile that the ligand may be added to these alkoxides before these form alkoxy bridges and get polymerized. Therefore, in addition to thiol and supporting electrolyte, 1.0 g of the ligand (1,10 - phenanthroline or 2,2’ - bipyridyl) was also added to these systems and the solution was electrolyzed at antimony anode and inert platinum cathode for ten hours. The products obtained are insoluble in commonly used organic solvents and do not melt upto 300^{0}C. Elemental analysis and infrared data conform to general formula, $Sb(SR)_3.L$.

Keywords: Antimony, Thiols, Tetrabutylammonium chloride

Introduction:

Electrochemical synthetic technique 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 sixteen decades. The first useful organo synthesis was made by Faraday[9] by electrolysing 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[23-28].
In view of the fact that the electrochemical methods provide unique route for the synthesis of a large variety of chemical compounds and the technique is associated with several advantages over the conventional synthetic methods, it was, therefore, considered worthwhile to explore the use of this technique for the synthesis of inorganic and organoantimony compounds. Antimony is chosen for present studies as its compounds play very important role in our daily life, medicines and industry.

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 by elemental analysis, Infrared spectral studies and other physical measurements. Efforts are also done to throw light on the mechanism of these reactions.

Experimental:

As the ligand (1,10-phenathroline or 2,2-bipyridyl) could not be added to the products of the above electrochemical reactions by refluxing for sufficiently prolonged period of time, therefore, coordination compounds of antimony(III) thiolates have been synthesized electrochemically. Electrochemical cell may be represented as:

$$Sb_{(+)} \left| \begin{array}{c} RSH \\ +CH_3CN + Bu_4NCl \\ + L \end{array} \right| Pt_{(-)}$$

All the symbols have their usual meanings. The electrochemical characteristics of these reactions are summarized in Table-I. After ten hours of electrolysis, light brown products separated in the anode compartment. These electrochemical products are quite stable and are not much affected by air and moisture. All these products are insoluble in various organic solvents. Molecular weight of these products could not be determined due to their insolubility in solvents. Melting point measurements of these products reveal that these do not melt upto a temperature of 300^{0}C. However, a change of the colour was observed in the temperature range of 200 – 250^{0}C which may be due to the decomposition of these products.

Antimony, carbon, hydrogen and sulphur contents in these products are determined and are listed in Table-I. Perusal of Table-I reveals that analytical data conform to molecular formula $Sb(SR)_3.L$.
Procedure for Elemental Analysis and Determination of Current Efficiency:

Elemental analysis:-

The elemental analysis (carbon, hydrogen, nitrogen, chlorine and bromine) of these products have been carried out by using Perkin - Elmer 2400 CHN elemental analyzer.

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 two hours. 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 % (say)

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

$$= 144 \text{ coulombs}$$

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

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

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

Result and Discussion:

A close inspection of the infrared spectral data reveals that these products do not show any absorption band in the region of 2603 – 2499 cm^{-1} indicates that the proton of thiol molecules is replaced in these reactions also[29]. However, the characteristic bands appear in the regions of 1605 – 1585 cm^{-1}, 660 – 653 cm^{-1}, 535 – 528 cm^{-1} and 462 – 456 cm^{-1}.
As discussed above the bands in the regions of 660 – 653 cm^{-1}, 535 – 528 cm^{-1} and 462 – 456 cm^{-1} can be assigned to ν(C – S), ν(Sb – S) terminal and ν(S – Sb – S) bridged stretching vibrations[30-31] respectively. Comaprison of the infrared data with that of the parent antimony(III) thiolates reveals that all these bands of present products appear in slightly higher regions. Shift of ν(C – S) and ν(Sb – S) bands to higher regions indicates the coordination of the ligand to antimony(III) thiolates.
Additional bands observed in the infrared spectra of these products in the region of 1605 – 1585 cm^{-1} may be due to the ligand molecules and can be assigned to ν(C ··· N) and ν(C ··· C) stretching vibrations[29-31]. These bands also appear at slightly higher region as compared to those in the infrared spectra of the pure ligand molecules[149].
Presence of ν(C ··· N) and ν(C ··· C) bands in the infrared spectra of these products and shift of all these bands (ν(C – S)Sb, ν(Sb – S), ν(S – Sb – S), ν(C ··· N) and ν(C ··· C)) towards higher region which confirm the coordination of the ligand~~s~~ to antimony(III) thiolates. Appearance of bridged ν(S – Sb – S) stretching vibrations, insoluble behaviour in various organic solvents and high melting point indicate that the present products are also polymeric in nature.

Current efficiencies of all these systems have also been determined and are listed in Table-I. The current efficiencies of these systems are quite high (0.78 – 0.97 g-eq F^{-1}). High current efficiencies of these systems show that the formation of the coordination compounds of antimony(III) thiolates are the predominant reactions of these systems. The reaction scheme for the formation of the products is given below:

At cathode:

$$3RSH + 3e^- \longrightarrow 3RS^- + \frac{3}{2}H_2\uparrow$$

At Sacrificial anode:

$$3RS^- + L + Sb_{(+)} \longrightarrow Sb(SR)_3.L + 3e^-$$

The present electrochemical technique given as unique route for the synthesis of antimony(III) thiolates and their coordination compounds. It is a direct single step and one - pot synthetic method which proceeds with very high current efficiencies.

Table-I: Electrolysis Characteristics, Analytical and other Related Data of Electrolysis of Thiols + Ligand Systems at Antimony Anode

System	Potential applied (V)	Electricity passed (Coulombs)	Product	Colour	Elemental analysis Found (Calc.) %				Current efficiencies (Gram-equivalent/ Faraday)
					Sb	C	H	S	
1-Methylpropane-1-thiol + 1,10-phenanthroline	40	720	$C_{12}H_{30}S_3SbC_{12}H_8N_2$	Light Brown	21.1 (21.29)	49.2 (50.37)	6.32 (6.64)	16.4 (16.79)	0.94
2-Methylpropane-2-thiol + 1,10-phenanthroline	60	720	$C_{12}H_{27}S_3SbC_{12}H_8N_2$	Light Brown	21.3 (21.40)	49.7 (50.37)	6.05 (6.12)	16.2 (16.7)	0.97
Pentane-1-thiol + 1,10-phenanthroline	50	720	$C_{15}H_{33}S_3SbC_{12}H_8N_2$	Light Brown	19.4 (19.93)	52.8 (53.04)	6.24 (6.71)	15.2 (15.71)	0.84
Propane-2-thiol + 1,10-phenanthroline	40	720	$C_9H_{24}S_3SbC_{12}H_8N_2$	Light Brown	22.68 (22.95)	47.23 (47.54)	5.57 (6.08)	17.91 (18.14)	0.91
Butane-1-thiol + 1,10-phenanthroline	50	720	$C_{12}H_{27}S_3SbC_{12}H_8N_2$	Light Brown	21.18 (21.37)	50.27 (50.61)	5.97 (6.19)	16.74 (16.89)	0.81
1-Methylpropane-1-thiol + 2,2′-Bipyridyl	40	720	$C_{12}H_{30}S_3SbC_{10}H_8N_2$	Light Brown	21.8 (22.22)	47.9 (48.19)	6.43 (6.93)	17.2 (17.52)	0.87
2-Methylpropane-2-thiol + 2,2′-Bipyridyl	30	720	$C_{12}H_{27}S_3SbC_{10}H_8N_2$	Light Brown	21.4 (22.34)	48.1 (48.46)	6.21 (6.42)	17.4 (17.6)	0.93
Pentane-1-thiol + 2,2′-Bipyridyl	50	720	$C_{15}H_{33}S_3SbC_{10}H_8N_2$	Light Brown	20.3 (20.74)	50.7 (51.12)	6.72 (6.98)	16.2 (16.36)	0.78
Propane-2-thiol + 2,2′-Bipyridyl	50	720	$C_9H_{24}S_3SbC_{10}H_8N_2$	Light Brown	23.28 (23.94)	44.37 (44.88)	6.21 (6.34)	18.34 (18.92)	0.96

Butane-1-thiol + 2,2′-Bipyridyl	60	720	$C_{12}H_{27}S_3SbC_{10}H_8N_2$	Light Brown	22.08 (22.31)	48.27 (48.43)	6.23 (6.41)	17.42 (17.64)	0.81

Table-II: Selected Infrared Absorption Bands of Products of Electrolysis of Thiols + Ligand Systems at Antimony Anode

System	Absorption band (cm^{-1})	Possible assignment
1-Methylpropane-1-thiol + 1,10-phenanthroline	462(s) 532(s) 658(s) 1605(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
2-Methylpropane-2-thiol + 1,10-phenanthroline	457(s) 535(s) 660(s) 1602(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
Pentane-1-thiol + 1,10-phenanthroline	458(s) 528(s) 658(s) 1595(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
Propane-2-thiol 1,10-phenanthroline	456(s) 532(s) 660(s) 1604(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
Butane-1-thiol + 1,10-phenanthroline	462(s) 532(s) 660(s) 1585(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
1-Methylpropane-1-thiol + 2,2′-Bipyridyl	462(s) 531(s) 653(s) 1603(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
2-Methylpropane-2-thiol + 2,2′-Bipyridyl	460(s) 532(s) 660(s) 1605(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
Pentane-1-thiol + 2,2′-Bipyridyl	461(s) 535(s) 659(s) 1597(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
	462(s) 532(s) 658(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S)

Propane-2-thiol + 2,2′-Bipyridyl	1592(s)	$\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$
Butane-1-thiol + 2,2′-Bipyridyl	456(s) 532(s) 660(s) 1594(s)	ν(S – Sb – S) ν(Sb – S) ν(C – S) $\left\{\begin{matrix}\nu(C\overset{\cdots}{-}N)\\ \nu(C\overset{\cdots}{-}C)\end{matrix}\right\}$

REFERENCES

1. Jay D. Wadhawan, Frank Marken, Richard G. Compton, Steve D. Bull and Stephen G. Devis, *Chem. Commun.*, 87, **2001**.
2. D. Degner, *Top. Curr. Chem.,* 1, 14, **1998**.
3. J. Utely, *Chem. Soc. Rev.,* 157, 26, **1997**.
4. Eberhard Steckhan, *Angewandte Chemie International*, 683, 25, **1986**.
5. A. Jutand, kk Hii, M Thornton-Pert and J.M. brown, *Organometallic*, 18, **1999**.
6. S. Olivero and E. Duanch, Eur. *J. Org. Chem.*, 1885, **1999**.
7. A Gennaro, A.A. Isse and F. Maran, *J. Electroanal. Chem*., 124, 507, **2001**.
8. Tung Siu, Weizi and Andrei K. Yudin, *J. Comb. Chem*., 554, 3, **2001**.
9. M. Faraday, *Ann. Phys. (Leipzig)*, 438, 47, **1834**.
10. Kolbe, *J. Prakt. Chem*., 138, 41, **1847**.
11. A. Crum Brown and J. Walker, *Liebigs Ann. Chem*., 107, 261, **1891**.
12. A. Crum Brown and J. Walker, *Liebigs Ann. Chem*., 41, 274, **1873**.
13. C. K. Maan and K.K. Bains, "*Electrochemical reactions in non-aqueous system*," Marcel-Dekker Inc., N.Y. **1970**.
14. H. Lund, K. Dassbjerg, D. Occhialini and S.U. Pedersen, *Elektrokhimiya*, 939, 31, 1995.
15. A. Jutand, S. Negri, *Eur. J. Org. Chem*., 1811, **1996**.
16. H. Lund, *Acta Chem. Scand*., 491. 1329. 11. **1957**.
17. N. Clauson-Kaas, F. Limborg and K. Glens, *Acta Chem. Scand*., 531, 6, **1952**.
18. L. Eberson and H. Schaffer, "Topic in current chemistry," No. 21, *Springer-Verlang Marlin Heidelberg*, N.Y. pp. (a) 144-154 (b) 49-58.
19. Tae-Hun Kim and Su Moon Park, *Electrochemica Acta*, 1461, 50, **2005**.
20. Aleksanda Buzarovska, Irena arsovaand Ljubomir Arsov, *J. Serb.Chem. Soc.*, 27-37, 66, **2001**.
21. T. Komoti and T. Nonaka, *J. Am. Chem. Soc.*, 2656, 106, **1984**.
22. T. Osa, Y. Kashiwangi, Y. Yanagisawa and J.M. Bobbit, *J. Chem. Soc. Chem. Commun.*, 2535, **1994**.
23. B.L. Funt and K.C. Yu, *J. Polym. Sci*., 359, 69, **1962**.
24. C. Simionescu and M. Grovu, *Angew. Markromol. Chem*., 149, 111, **1983**.
25. G.S. Shapoval, *J. Macromol. Sci. chem*., 453, A 17, **1982**.
26. J.H. Simons, *J. Electrochem. Soc*., 47. 95, **1949**.
27. H.A. Rehan, *Polymer International*, 218-224, 52, **2003**.
28. Youichi Tsuchiya and Hisashi Fujihara, *Electrochemistry*, 584, 70, **2002**.
29. Prem Raj, Santosh Agnihotri, and Kiran Singhal, *Synth. React. Inorg. Met-Org., Chem*., 569–581, 32(3), **2002**.
30. Taimur A. Shaikh, Sean Parkin, David A. Atwood, *Journal of Organometallic Chemistry* 4167–4171, 691, **2006**.
31. Rakesh Bohra, Anita Dhammani, Rajnish K. Sharma and Ram C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem*., 681– 693, 31(4), **2001**.