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Research Article

Direct Electrochemical Synthesis of Bismuth (III) Carboxylates and their Coordination Complexes.

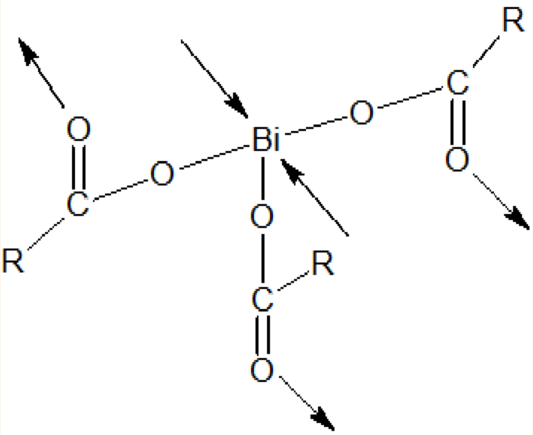
Baljit Singh*, Shavina and Kanchan Bala

Department of Chemistry, Punjabi University, Patiala-147002, Punjab, India.

Abstract

Bismuth (III) carboxylates $Bi(OOCR)_3$ have been prepared by the electrochemical oxidation of sacrificial bismuth anode in acetonitrile containing carboxylic acid RCOOH (R= CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17} and C_9H_{19}). On refluxing with nitrogen containing ligand β–picoline, these carboxylates do not form coordination compounds. However, the coordination compounds with general formula $Bi(OOCR)_3.L$, (L: β-picoline) have been successfully synthesized electrochemically by addition of this ligand to the electrolysis phase. All these products have been characterized by elemental analysis, infrared spectral studies and other physical measurements. The current efficiencies of all these systems are quite high.

Keywords: Electrochemical oxidation, Sacrificial bismuth anode, Bismuth (III) carboxylates, Coordination compounds and Current efficiencies.



***Correspondence**
Baljit Singh,
Email: baljit_chemz@yahoo.co.in

Introduction

The electrochemical technique is a simple, rapid, selective and one pot method to achieve the oxidation and reduction without introducing any foreign oxidizing or reducing agent. It covers a broad spectrum of application in organic [1-4], inorganic [5-6] and green chemistry [7]. It has a large variety of applications in textile (such as manufacturing fibres, dyeing processes and decolourizing fabrics) industries [8], pharmaceutical industries [9] and chemical industries [10]. It is an attractive procedure for the preparation of the metal complexes by electrochemical dissolution of sacrificial metal anode. So, we have now extended this direct electrochemical synthesis method for the preparation of bismuth (III) carboxylates and their adducts with the ligand β–picoline.

Experimental

Material and Equipment

Acetonitrile was dried over phosphorous pentoxide for 24 hours and then double distilled. The freshly distilled acetonitrile was used as a solvent. Tetrabutylammonium chloride was crystallised from conductivity water, dried under reduced pressure at $100^{o}C$ and was used as a supporting electrolyte. Carboxylic acids were used as supplied (Merck). Electrolysis was carried out in an H-type cell made up of pyrex glass in which two compartments anodic and cathodic were separated from each other by a sintered glass disc of G-4 porosity. Platinum foil (1.0 x 1.0 cm^2) was used as inert cathode and bismuth rod (2.0 x 10 x 0.2 cm^3) as sacrificial anode. Direct current for electrochemical oxidation was obtained by using Toshniwal electrophoresis power supply.

Electrochemical Procedure

To synthesize bismuth(III) carboxylates, a reaction mixture of 4.0 mL of carboxylic acid (RCOOH) in 250 mL of acetonitrile using tetrabutylammonium chloride (1.0 g) as supporting electrolyte was prepared and then the whole reaction mixture was put into the H-type electrolytic cell. The sacrificial bismuth electrode and inert platinum electrode were introduced in the anodic and cathodic compartments of H-type cell respectively. The electrolytic cell was closed from both sides with the help of guard tubes (filled with dried calcium chloride and glass wool) so as to protect the reaction mixture from moisture. Necessary connections were made with the electrophoresis power supply of Toshniwal make. The potential across the electrodes was so adjusted that a current of 20mA passed through the solution. The reaction mixture was stirred effectively with the magnetic bead using magnetic stirrer in order to remove the product adhering on the electrode.

The cell can be represented as:

$$\mathrm{Bi}_{(+)}\left|\begin{array}{c}\mathrm{RCOOH + Bu_4NCl}\\ \mathrm{+\ CH_3CN}\end{array}\right|\mathrm{Pt}_{(-)}$$

Where,
$\mathrm{Bi}_{(+)}$ is sacrificial bismuth anode
$\mathrm{Pt}_{(-)}$ is inert platinum cathode
$\mathrm{Bu_4NCl}$ is tetrabutylammonium chloride
RCOOH is carboxylic acid used in the systems.

Electrolysis was conducted for 10 hours at a constant current of 20mA, so that a sufficient amount of product may be obtained in the anodic compartment. The solid product separated in the anodic compartment was filtered and washed with warm acetonitrile, dry diethyl ether and then finally dried under vacuum. All efforts were done to protect the product from air and moisture.

For the synthesis of coordination compounds of these products electrochemically, 1.0 mL of ligand $\beta-$picoline was also added in addition to above substrates before starting the electrolysis and electrolysis have been done under the similar conditions.

Melting point of all these products was determined using electrical device with a heating rate of 5^{o}C per minute. Bismuth contents in all these compounds were determined using oxine method [11]. Carbon, hydrogen and nitrogen (where applicable) contents in the products were determined through ‘Elementor Vario EL’ CHNS elemental analyser.

Infrared spectra of the products have been recorded on Perkin-Elmer spectrophotometer (FTIR) in the region of 4000-400 cm^{-1} using KBr pallets. The current efficiencies [12] (Gram Equivalents of metal dissolved per Faraday of electricity passed) of all these reactions were determined using Faraday’s first law of electrolysis by electrolyzing the above systems for exactly two hours at a constant current of 20mA. After the electrolysis of 2.0 hours, the solution in anode compartment was distilled in rotary film evaporator (Buchi) till 10 mL of content was left in the flask. The contents were transferred to the beaker and heated to dryness. The bismuth contents were then determined volumetrically in the dry mass by oxine method. The theoretical value of bismuth was calculated by using Faraday’s first law of electrolysis. The ratio of experimental and theoretical bismuth contents gives the electrochemical efficiency or current efficiency of the system.

Results and discussion

(i) Bismuth carboxylates

Electrochemical reactions of above said carboxylic acids at sacrificial bismuth anode and inert platinum cathode yield bismuth (III) carboxylates. The mechanism of the reaction is given below:

At inert cathode:

$$3RCOOH + 3e^- \longrightarrow 3RCOO^- + 3/2\ H_2\uparrow$$

At sacrificial anode:

$$3RCOO^- + Bi_{(+)} \longrightarrow Bi(OOCR)_3 + 3e^-$$

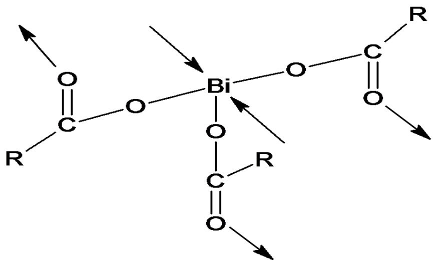
It has been observed that these products do not melt upto 300°C but decompose at a temperature around 220-250°C. The decomposition of the products is indicated from the change in colour of these compounds. These products are not much affected by air or moisture. All these compounds are insoluble in most of commonly used organic solvents like methanol, ethanol, acetone, benzene, chloroform, carbon tetrachloride, N,N'-dimethyl formamide, pyridine and carbon disulphide etc. Elemental analysis of bismuth (oxine method), carbon, hydrogen and other analytical data suggests the 3:1 stoichiometry ratio of carboxylic acid and bismuth which conforms to molecular formula $Bi(OOCR)_3$. All the relevant data is summarized in **Table-I.**

Infrared spectra of all these products reveals that there is no broad absorption band due to the hydroxyl group of the carboxylic acid i.e. in the region of 3300-2800 cm^{-1} which confirms the deprotonation. However, characteristic bands of these compounds appeared in the region of 1525-1505 cm^{-1}, 1406-1332 cm^{-1} and 695-536 cm^{-1}.

It is reported in literature that ν(C=O) of carboxylic group appears in the range of 1725-1700 cm^{-1} in free carboxylic acids. In literature [13], in the region of 1650-1300 cm^{-1}, the stretching vibrations of carboxylates ion (ν_{asym} and ν_{sym}) are reported. It is also reported in literature [14-15] that in metal carboxylates, $\nu(COO^-)$ anti-symmetric and $\nu(COO^-)$ symmetric stretching vibrations appear in the region of 1600-1510 cm^{-1} and 1410-1330 cm^{-1} respectively.

In the present electrochemical products, there is no peak observed in the range of 1725-1700 cm^{-1}, which indicates that there is no free carbonyl group of carboxylic acids. It is reported [16] that in metal complexes, ν(C=O) peak gets lowered substantially. So, in the present electrochemical products, this ν(C=O) peak of the carboxylic group is drastically decreased and gives rise to absorption bands in the region of 1525-1505 cm^{-1} and 1406-1332 cm^{-1} showing thereby the carboxylic group is coordinated to bismuth metal and these absorption bands were assigned to asymmetric and symmetric vibrations of carboxylate $\nu(COO^-)$ group.

It has also been reported [17-18] in the literature that ν(M-O) stretching vibrations in general appear in the region of 600-400 cm^{-1} and ν(Bi-O) [19] stretching vibrations in the region of 550-540 cm^{-1}. Thus, in the present electrochemical products, the bands appeared in the region of 695-536 cm^{-1} are assigned to the ν(Bi-O) stretching vibrations. An interesting feature of these absorption bands is that these bands are comparatively broad showing the bridging structure and it also confirms that these compounds may be polymeric in nature. The plausible structure of these unique polymeric bismuth (III) carboxylates is shown below:



The current efficiencies of these electrochemical reactions have also been determined and are recorded in **Table 1**. It has been observed that the current efficiencies of all these systems are quite high except propanoic acid system.

Many organic compounds have been reported [17,20-21] to behave as corrosion inhibitors for metal surfaces. Comparatively low current efficiency of the reaction of propanoic acid at the bismuth anode may be due to corrosion inhibiting behaviour of this carboxylic acid or its bismuth compound on the bismuth metal surface. In order to throw some light on the mechanism of corrosion inhibition of this system, current efficiency of propanoic acid system has been determined at different intervals of time and is listed in **Table 2**. Perusal of Table 2 shows that the current efficiency of this system is high at the initial stage and decreases with the passage of time. The decrease in current efficiency indicates that this compound forms a protective layer around the sacrificial bismuth metal and hence acts as corrosion inhibitor.

Table 1 Electrolysis characteristics, analytical and other related data of electrolytic products of carboxylic acids at sacrificial bismuth anode (Potential: 50V, Current in Coulombs: 720)

System	**Product**	**Colour**	**Elemental Analysis found (calculated)%**				**Current efficiency (gram equivalent/ Faraday)**
			Bi	**C**	**H**	**N**	
Ethanoic acid	$BiC_6H_9O_6$	White	54.0 (54.4)	18.5 (18.7)	2.0 (2.3)	---	0.65
Propanoic acid	$BiC_9H_{15}O_6$	White	48.2 (48.8)	25.0 (25.2)	3.4 (3.5)	---	0.46
Butyric acid	$BiC_{12}H_{21}O_6$	White	44.2 (44.5)	30.2 (30.6)	4.3 (4.5)	---	0.75
Pentanoic acid	$BiC_{15}H_{27}O_6$	Light Green	39.9 (40.8)	35.0 (35.2)	5.1 (5.3)	---	0.90
Hexanoic acid	$BiC_{18}H_{33}O_6$	White	37.5 (37.7)	38.8 (39.0)	5.8 (6.0)	---	0.98
Heptanoic acid	$BiC_{21}H_{39}O_6$	Cream	35.0 (35.1)	42.0 (42.3)	6.2 (6.5)	---	0.92
Octanoic acid	$BiC_{24}H_{45}O_6$	Cream	31.9 (32.8)	44.8 (45.1)	6.9 (7.1)	---	0.69
Nonanoic acid	$BiC_{27}H_{51}O_6$	White	30.0 (30.7)	47.3 (47.6)	7.3 (7.5)	---	0.82
Decanoic acid	$BiC_{30}H_{57}O_6$	White	28.5 (28.9)	49.6 (49.9)	7.6 (7.9)	---	0.86
Ethanoic acid + β-picoline	$BiC_6H_9O_6 .C_6H_7N$	White	43.2 (43.6)	29.9 (30.1)	3.1 (3.3)	2.7 (2.9)	0.91
Propanoic acid + β-picoline	$BiC_9H_{15}O_6.C_6H_7N$	White	39.6 (40.1)	34.1 (34.5)	4.0 (4.2)	2.5 (2.7)	0.97
Butyric acid +β-picoline	$BiC_{12}H_{21}O_6.C_6H_7N$	White	36.9 (37.1)	38.2 (38.4)	4.7 (5.0)	2.2 (2.5)	0.98
Pentanoic acid + β-picoline	$BiC_{15}H_{27}O_6.C_6H_7N$	White	34.3 (34.5)	41.3 (41.6)	5.3 (5.6)	2.0 (2.3)	0.95

Hexanoic acid + β-picoline	$BiC_{18}H_{33}O_6.C_6H_7N$	Cream	32.0 (32.3)	44.3 (44.5)	6.0 (6.2)	1.9 (2.2)	0.71
Heptanoic acid +β-picoline	$BiC_{21}H_{39}O_6.C_6H_7N$	White	30.0 (30.3)	46.8 (47.0)	6.4 (6.7)	1.8 (2.0)	0.92
Octanoic acid + β-picoline	$BiC_{24}H_{45}O_6.C_6H_7N$	Light Green	28.4 (28.6)	49.0 (49.2)	6.9 (7.1)	1.8 (1.9)	0.80
Nonanoic acid + β-picoline	$BiC_{27}H_{51}O_6.C_6H_7N$	Cream	26.8 (27.0)	51.1 (51.2)	7.3 (7.5)	1.5 (1.8)	0.89
Decanoic acid + β-picoline	$BiC_{30}H_{57}O_6.C_6H_7N$	Light Brown	25.4 (25.6)	52.6 (52.9)	7.5 (7.9)	1.5 (1.7)	0.69

Table 2 Current efficiencies of the electrochemical reaction of propanoic acid at bismuth anode at different intervals of time

System	Time (in hours)	Current efficiency (gram equivalent/ Faraday)
Propanoic acid	1.0	0.90
	1.5	0.75
	2.0	0.46

(ii) Coordination compounds of bismuth (III) carboxylates:

The bismuth (III) carboxylates prepared have been refluxed with β–picoline in polar and non-polar solvents like methanol, ethanol, benzene and acetonitrile for 48 hours in order to prepare coordination compounds of these bismuth carboxylates. However the analytical and IR data of these compounds showed that the ligand molecule could not be attached to these bismuth (III) carboxylates. It may be due to the reason that the metal atom in these carboxylates have already achieved its favourable coordination number through carboxylate bridging, therefore, further expansion of coordination sphere due to the addition of ligand could not be achieved. It was thus considered worthwhile that the ligand may be added to these carboxylates before these form carboxylate bridging and get polymerized. So, it was thought that the ligand molecule can be added electrochemically. So, the coordination compounds of these bismuth (III) carboxylates have been prepared by adding 1.0 mL of β–picoline in addition of the supporting electrolyte and reactant before starting the electrolysis process. The other details were essentially the same as discussed earlier for the synthesis of bismuth (III) carboxylates.

The cell can be represented as:

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

Where, L: Ligand β-picoline and the other symbols have the same meanings as discussed earlier.

The elemental analysis of bismuth (oxine method), carbon, hydrogen and nitrogen in these products are in good agreement with 3:1:1 stoichiometry of carboxylic acid, bismuth and ligand respectively and corresponds to the general molecular formula $Bi(OOCR)_3.L$ and the analytical data is listed in **Table 1**.

IR spectra of metal complexes with ligand β-picoline shows that there is no ν(O-H) peak of carboxylic acids which indicates deprotonation. However, characteristic bands appeared in the region of 1538-1515 cm^{-1}, 1415-1352 cm^{-1}. These coordination compounds show the absorption like their parent compounds in the respective regions with only difference that these bands appear slightly in the higher region (+10 to 20 cm^{-1}). Also the ν(C=O) stretching vibration in the coordination compounds of carboxylic acids gets lowered and give rise to absorption bands in the region of 1538-1515 cm^{-1} and 1415-1352 cm^{-1}. These peaks are assigned to ν(COO^-) asymmetric and ν(COO^-) symmetric stretching vibrations respectively. Moreover, $\nu\ (C\overset{\cdots}{-}C)/\ \nu\ (C\overset{\cdots}{-}N)$ bands in the region of 1570-1465 cm^{-1} also appeared in these compounds due to ligand molecule which are present at comparatively lower region than the pure ligand [22]. This is due to the complexation of the ligand molecule with bismuth metal. These bands were completely absent in parent bismuth (III) carboxylates and thereby confirming that the ligand molecule has been added.

The current efficiencies of these systems (presented in Table-I) are also quite high (in the range of 0.69 to 0.98 gram equivalents per Faraday) showing the reactions leading to the formation of coordination compounds of bismuth (III) carboxylates are the predominant reactions of these systems.

The reaction scheme may be written as:

At inert cathode:

$$3RCOOH + 3e^- \longrightarrow 3RCOO^- + 3/2H_2$$

At sacrificial anode:

$$3RCOO^- + L + Bi_{(+)} \longrightarrow Bi(OOCR)_3.L + 3e^-$$

Conclusion

The present electrochemical method of the synthesis of bismuth (III) carboxylates and their coordination compounds is direct, simple and one pot as compared to the classical multistep methods for the synthesis of metal carboxylates. Current efficiency of all these systems is quite high. So, the technique offers a versatile approach for the commercial preparation of these compounds.

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References

[1] J.D. Wadhawn, F. Marken, R.G. Compton, S.D. Bull and S.G. Davies, *Chem. Commun*; **2001**, 87.
[2] A. Jutand, KK Hii, M.T. Pett. and J.M. Brown, *Organometallic*; **1999**, 18.
[3] H.A. Rehan, *Polymer International;* **2003**, 52, 218.
[4] Y. Tsuchiya and H. Fujihara, *Electrochemistry*; **2002**, 70, 584.
[5] N. A. Bell, W. Clegg, J. R. Creighton, *Inorg. Chim. Acta*; **2000**,303,12.
[6] N. A. Bell, W. Clegg, *Inorg. Chim. Acta*; **2000**, 303, 220.
[7] F. Liu, S. Liu, Q. Feng, S.X. Zhung, J. Jhang, P. Bu, *Int .J. Electrochem. Sci;* **2012**, 7, 4381.
[8] M. Sala and M.C.G. Bouzan, *International Journal of Photo Energy*; **2012**, 2012.
[9] S. Kumar and D.P. Srivastava, *Indian J. Pharm Sci*; **2010**, 72(4), 458.
[10] S.H. Hosseini, M. Dabiri and M.A. Shrafi, *Polymer International* ; **2006**, 55, 1081.
[11] Vogel's, "*Text Book of Quantitative Chemical Analysis*", Longman Group UK, Ltd; 1989.
[12] B. Singh, K. Bala, S. Singh and K. Singh, *Chem. Sci. Trans*; **2013**, 2(4), 1312.
[13] M.S. Refat, S.A.EI-Korashy and M.A. Hussien, *Can. Chem. Trans*; **2014**, 2(1), 24.

[14] O. Anjaneyulu and K.C.K. Swamy, *J. Chem. Sci*; **2011**, 123,131.

[15] D. Sakthilatha and R. Rajavel, *Chem .Sci. Trans*; **2013**,2(3),711.

[16] M. Ibrahim, A. Nada, D.E. Kamal, *Indian J. Pure and Appl Phys;* **2005**, 43, 911.

[17] B. Singh and K. Bala, *J. Indian Chem. Soc*; **2011**, 88, 271.

[18] A.S. Aldwayyan, F.M.Al-Jekhedab, M.Al-Noaimi, B. Hammouti, T.B. Hadda, M. Sulliman, I. Warad, *Int. J. Electrochem. Sci*; **2013**, 8, 10506.

[19] B. Singh and H. Kaur, *J. Indian Chem. Soc*; **2008**, 85, 849.

[20] B. Singh, K. Bala, K. Singh and S. Singh, *Journal of Advances in Chemistry*; **2013**, 5, 592.

[21] J.S. Banait, B. Singh and S. Rala, *J. Indian Chem. Soc.*; **2007**, 84, 135.

[22] M.T.H. Tarafder, T.J. Khoo, K.A. Crouse, A.M. Ali, B.M. Yamin, H.K. Fun, *Polyhedron*, **2002**, 21(27-28), 2697.

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