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ELECTROCHEMICAL SYNTHESIS OF ANTIMONY(III) GLYCOLATES

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ABSTRACT

Electrochemical reactions of acetaldehyde, benzaldehyde, salicylaldehyde, cinnamaldehyde, propionaldehyde, acetone, ethyl methyl ketone and isobutyl methyl ketone 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 to be Antimony (III) glycolates. All these reactions proceed with high current efficiencies.

KEY WORDS

Antimony, acetonitrile, tetrabutylammonium chloride, aldehydes, keones

INTRODUCTION

This technique deals with the reactions proceeding at the expense of external electrical energy. It has been used as a synthetic method in organic chemistry for the last sixteen decades. The first useful organo synthesis was made by Faraday 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 in 1847. The use of this technique in organic synthesis was later extended by Brown and Walker. These were followed by the development of a number of reactions such as coupling reactions, substitution reactions, electron transfer reactions, conversion reactions, polymerization reactions and chiral induction reactions. Some of these reactions were also used on industrial scale[1-10].

Antimony and its compounds play important role in our daily life. Antimony compounds have been employed medicinally since ancient times. Trivalent organoantimony compounds have been used in a wide variety of reactions such as self-coupling reactions, cross-coupling reactions. Optically active organoantimony compounds are utilized for asymmetric synthesis, i.e., synthesis of optically active antimony compounds. Antimony compounds also exhibit significant biological activity[11], catalytic oxidation[12], antimicrobial, antitumor activities[13], antileishmanial activity[14] as well as cytostatic activities[15].

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 very important role in our daily life, medicines and industry[16-19].

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 reveals[1-10] that this technique is associated with several advantages over the conventional synthetic methods. In the light of above advantages, I am discussing electrochemical synthesis and characterization of antimony (III) glycolates and their coordination compounds.

EXPERIMENTAL:

Apparatus used

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 x 1.0 cm^2) and antimony sheet (2.0 x 10 x 0.2 cm^3) were used as cathode and anode respectively. The electrolytic solution in the anode compartment was stirred efficiently using magnetic stirrer.

Power Supply: -

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.

Magnetic Stirrer: -

Electrolytic solution stirred with the help of magnetic stirrer (Perfit). Magnetic bead sealed with Teflon was used for stirring.

Infrared Spectrophotometer: -

Infrared spectrum recorded with using potassium bromide pellets in the region of 4000 – 450 cm^{-1}.

Melting Point Device: -

Melting point of the products was measured by using electrical device of 'Perfit'

Reagents, their Purification

Acetone: -

Acetone (Extra pure) was purified by adding the solution of silver nitrate (3 g in 20 mL of distilled water) and 20 mL of normal sodium hydroxide in 700 mL of acetone. This mixture was shaken for ten minutes, filtered, dried over anhydrous calcium chloride and distilled. The fraction coming out at 56.2^{0}C/760 mmHg was collected.

Acetonitrile: -

Water may be removed from acetonitrile (Merck) by adding activated silica gel or Type 4-A molecular sieves. To the partially dried solvent, calcium hydride was added portion wise until hydrogen evolution ceases. The solvent was then decanted from the solid and fraction distilling at 82^{0}C/760 mmHg was collected.

Diethyl ether: -

Diethyl ether (Fluka) of analytical reagent grade was refluxed with sodium metal for twenty-four hours. The fraction distilling at 34^{0}C was collected and kept over sodium wire.

Tetrabutylammonium chloride: -

Tetrabutylammonium chloride used as supporting electrolyte.

Electrochemical Reactions of aldehyde/ketones at Antimony Anode:

Decomposition potential (the potential at which the substrate loses electrons at the anode surface) of aldehyde/ketones was determined, which was found to be less than 1.5 V. Electrochemical reactions of the solution of these aldehyde/ketones 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 hours. 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 milli 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 (1.0 g) was carried out. The electrolytic cell can be represented as:

$$Sb_{(+)} \;\big|\; \begin{matrix} RCHO/RCOR' \\ +CH_3CN + Bu_4NCl \end{matrix} \;\big|\; Pt_{(-)}$$

Where;

RCHO/ RCOR' represent aldehydes/ketones

The products are insoluble in commonly used organic solvents. Due to insoluble behavior, the molecular weight of these products could not be determined.

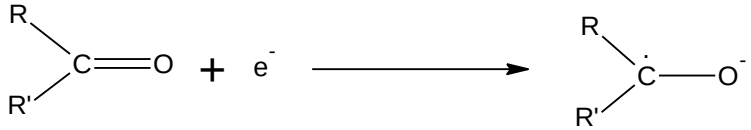
All these products do not melt up to 300^0C, however, color of these products changes in the temperature range 220^0C – 245^0C, thereby indicating that these products may decompose around this temperature. Analytical data (antimony, carbon and hydrogen contents in all the products) are summarized in Table-S1 and conform to the molecular formula, $Sb_2(OCHR)_6$ in case of aldehydes and $Sb_2(OC(R')\ R)_6$ in case of ketones. Infrared spectra of the products (enlisted in Table-S2) have been recorded in the region of 4000 – 450 cm^{-1} as discussed in previous chapters.

The products do not show any absorption band corresponding to carbonyl group[17] except in case of the product of salicylaldehyde. However, characteristic absorption bands in all these products appear in the regions of 1148 – 1000 cm^{-1} and 574 - 548 cm^{-1}.

Literature reveals[18] that in metal alkoxides ν (Sb – O) absorption bands appear in the region of 612 – 540 cm^{-1}. The presence of absorption bands in the region of 574 - 548 cm^{-1} thus can be assigned to ν (Sb – O) stretching vibrations.

Infrared spectra of the present electrochemical products show absorption bands in the region of 1060 – 1000 cm^{-1} due to bridged ν (C – O) Sb[19] alkoxide groups and 1148 – 1060 cm^{-1} due to ν (C – O) Sb terminal alkoxide groups.

Literature reveals[19] that reduction of aldehydes and ketones at inert cathode yield radical anions:



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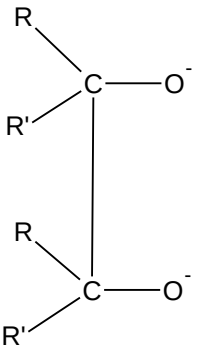
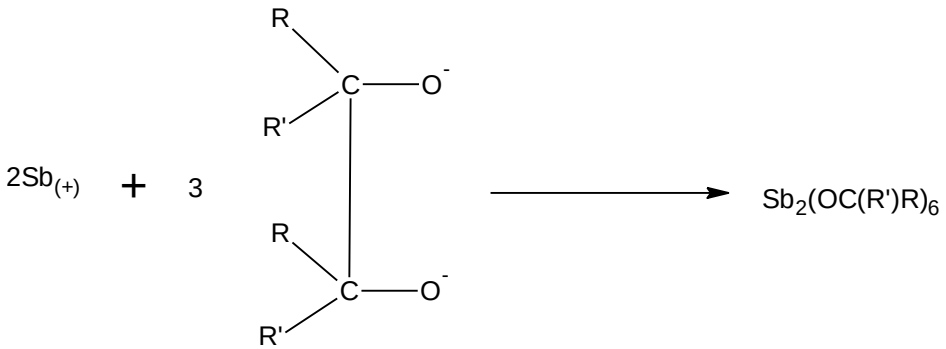
(Where R' represent hydrogen atom in case of aldehydes and alkyl groups in case of ketones)

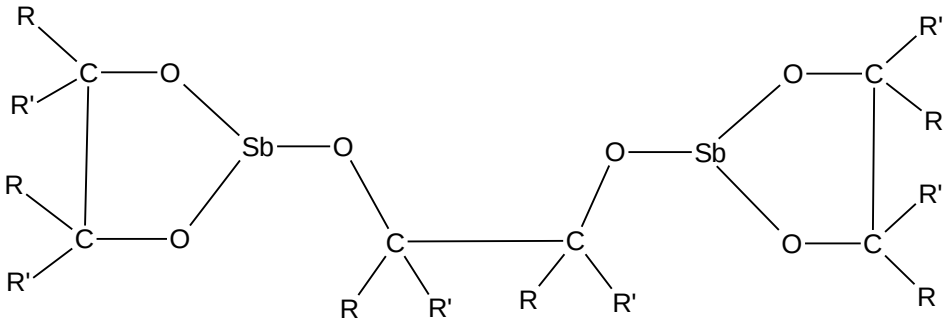
The radical anions dimerise to yield dianions;



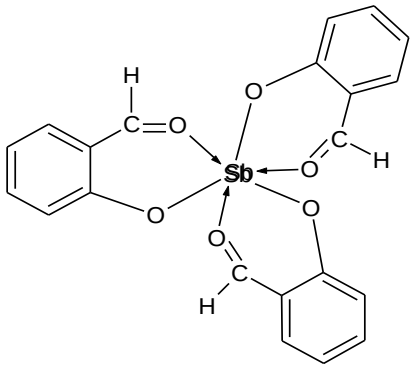
Under the influence of the applied potential these dianions move towards antimony anode to yield antimony (III) glycolates.



The plausible structure is given as:

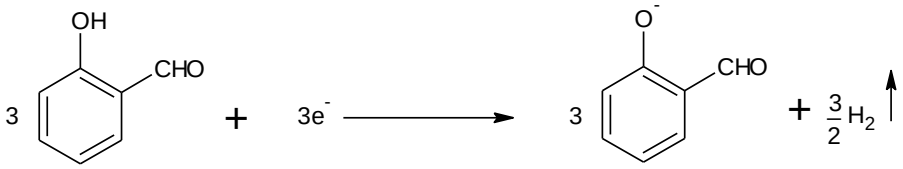


The product of salicylaldehyde at antimony anode is also insoluble in various organic solvents. The infrared data of this product show no absorption band due to ν (O – H)[20] functional group. However, there is an absorption band at 1720 cm^{-1} corresponding to ν (C = O) stretching vibrations[20]. The product also shows absorption bands at 1146 cm^{-1}, 1020 cm^{-1} and 574 cm^{-1} which can be assigned to terminal ν (C – O) Sb, bridged ν(C – O)Sb, and ν(Sb – O) stretching vibrations respectively. In this product additional bands appear at 2800 cm^{-1} and 2700 cm^{-1} due to interaction between C - H stretching fundamental and overtones of C – H deformation of aldehyde group[22]. The presence of bands in these two regions and band due to carbonyl group indicate that carbonyl group of salicylaldehyde do not take part in the reaction. The plausible structure is given as:

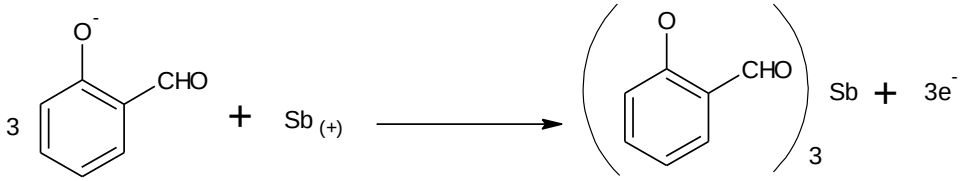


In case of of salicylaldehyde, the phenolic group is easily reducible than aldehyde group thus only phenolic group is reduced at inert cathode, the reaction scheme may be written as:

At Cathode:



At Anode:



Infrared spectral data, high melting point and insoluble behavior of the present products indicate that these products may be polymeric in nature.

Current efficiencies of these systems have also been determined and enlisted in Table-S1. Perusal of Table-1 reveals that current efficiencies of these systems are quite high. High current efficiencies of these systems indicate that reactions leading to the formation of antimony (III) glycolates are the predominant reactions of these systems.

Table-S1: Electrolysis Characteristics, Analytical and other Related Data of Electrolysis of Aldehydes and Ketones at Antimony Anode

System	Potential applied (V)	Electricity passed (Coulombs)	Product	Colour	Elemental analysis Found (Calc.) %			Current efficiencies (Gram-equivalent/ Faraday)
					Sb	C	H	
Acetaldehyde	40	720	$Sb(OC_2H_4)_3$	Light Brown	46.53 (47.98)	28.12 (28.37)	4.28 (4.72)	0.78
Benzaldehyde	40	720	$Sb(OC_7H_6)_3$	Light Brown	27.37 (27.68)	56.94 (57.30)	3.89 (4.09)	0.86
Salicylaldehyde	30	720	$Sb(O_2C_7H_5)_3$	Light Brown	25.03 (25.11)	51.24 (51.98)	12.15 (12.32)	0.94
Cinnamaldehyde	60	720	$Sb(OC_9H_8)_3$	Light Brown	23.47 (23.51)	62.27 (62.57)	3.95 (4.63)	0.97
Propionaldehyde	40	720	$Sb(OC_3H_6)_3$	Light Brown	40.94 (41.16)	35.48 (36.51)	5.47 (6.08)	0.81
Acetone	50	720	$Sb(OC_3H_6)_3$	Light Brown	40.87 (41.16)	36.17 (36.51)	5.36 (6.08)	0.91
Ethyl methyl ketone	30	720	$Sb(OC_4H_8)_3$	Light Brown	35.75 (36.04)	41.98 (42.63)	6.45 (7.10)	0.83
Isobutyl methyl ketone	50	720	$Sb(OC_6H_{12})_3$	Light Brown	27.85 (28.86)	50.79 (51.21)	8.17 (8.53)	0.74

Table-S2: Selected Infrared Absorption Bands of Products of Electrolysis of various Aldehydes and Ketones at Antimony Anode

System	Absorption band (cm^{-1})	Possible assignment
Acetaldehyde	548(s)	ν(Sb – O)
	1018(m)	ν(C – O)Sb
	1131(m)	ν(C – O)Sb
Benzaldehyde	564(s)	ν(Sb – O)
	1021(m)	ν(C – O)Sb
	1148(m)	ν(C – O)Sb
Salicylaldehyde	574(s)	ν(Sb – O)
	1020(m)	ν(C – O)Sb
	1146(m)	ν(C – O)Sb
	1720 (s)	ν(C = O)
	2700(s)	ν(C - H)
	2800(s)	ν(C - H)
Cinnamaldehyde	567(s)	ν(Sb – O)
	1026(m)	ν(C – O)Sb
	1128(m)	ν(C – O)Sb
Propionaldehyde	574(s)	ν(Sb – O)
	1060(m)	ν(C – O)Sb
	1115(m)	ν(C – O)Sb
Acetone	571(s)	ν(Sb – O)
	1023(m)	ν(C – O)Sb
	1134(m)	ν(C – O)Sb
Ethyl methyl ketone	567(s)	ν(Sb – O)
	1016(m)	ν(C – O)Sb
	1125(m)	ν(C – O)Sb
Isobutyl methyl ketone	573(s)	ν(Sb – O)
	1000(m)	ν(C – O)Sb
	1131(m)	ν(C – O)Sb

CONCLUSION:

Electrochemical technique is reported to exhibit several advantages over the conventional methods in synthetic organic chemistry. Present work is an effort to explore the use of this technique for the synthesis of inorganic compounds. Therefore, antimony glycolates have been synthesized electrochemically. The present studies reveal that in addition to the usual advantages associated with this technique in organic synthetic chemistry, the present electrochemical method represents a direct, single-step and single-pot route for the synthesis of inorganic compounds.

During the last decades, the use of pure metals as reagents has increased through the development of vapor phase synthetic technique. The requirement of such experiments includes an efficient high vacuum system of appreciable pumping capacity, some means of evaporating metals, a cold trap for the collection of products and some sophisticated instruments to identify the species produced. In contrast, the present electrochemical reactions are conducted at room temperature with all the advantages of using routine laboratory apparatus and equipment and metals as reagents. Additional advantage associated with this technique is that these proceed with very high current efficiencies.

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Supplementary data:

Supplementary data for the same is within the manuscript.

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