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Electrochemical Synthesis Of Antimony(III) Thiolates

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Abstract:
Electrolysis of 5.0 mL of the thiol (1-methylpropane-1-thiol, 2-methylpropane-2-thiol, pentane-1-thiol, propane-2-thiol and butane-1-thiol) 1.0 g of tetrabutylammonium chloride dissolved in 250 mL of acetonitrile was conducted in the H - type cell at antimony anode and inert platinum cathode by passing current of 20 mA. The light brown product separating in the anode compartment was isolated from the reaction mixture after ten hours of electrolysis. The product so obtained was washed with hot acetonitrile, dry ether and then finally dried under vacuum. Infrared spectra of the products have been recorded, Current efficiencies of all these systems have also been determined

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].

Review of literature reveals[1-28] that a variety of useful organic compounds have been synthesized electrochemically in last many years. However, the use of electrochemistry for the synthesis of inorganic as well as organometallic compounds[29-47] was developed during the past three decades. A close study of this technique reveals that the electrochemical synthetic technique has many advantages over the conventional synthetic methods as discussed below:

1. 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.
2. 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.
3. 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.
4. This method usually needs cheap starting material as the reaction can directly be conducted with metal instead of using its costly compounds.
5. This technique does not cause any pollution problem, thus is a keen step towards green chemistry[48-51].
6. The technique generally provides shortcut routes to multi-step reactions[1,10].
7. 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. Thus electrochemical reactions can be conducted at ambient temperatures.
8. The electrochemical reactions have low activation energy and hence these are fast reactions as compared to usual chemical reactions.

electrochemical reactions of 5.0 mL of a thiols (1-methylpropane-1-thiol, 2-methylpropane-2-thiol, pentane-1-thiol, propane-2-thiol and butane-1-thiol), 1.0 g of tetrabutylammonium chloride and 250 mL of freshly distilled acetonitrile were conducted in the H - type cell at a potential of 50 - 60 V. The cell can be represented as:

$Sb_{(+)}$ RSH +Bu_4NCl +CH_3CN $Pt_{(-)}$

Where:
$Sb_{(+)}$ is antimony anode
$Pt_{(-)}$ is platinum cathode.
Bu_4NCl is the supporting electrolyte
RSH is thiol used in the systems

Products isolated from the reaction mixture are quite stable and are not much affected by air and moisture. All these products are insoluble in various organic solvents such as methanol, ethanol, benzene, chloroform, carbon tetrachloride, N,N-dimethyl formamide, dimethyl sulphoxide, acetone, etc. The molecular weight of the products could not be determined due to their insoluble behaviour. These products do not melt up to 300^{0}C, however, it was observed that these compounds change their colour in the temperature range of 200 to 250^{0}C which indicates that these products decompose around this temperature.

Antimony contents in all these products were determined iodometrically[134]. Microanalysis for carbon and hydrogen contents of the products has also been carried out. The analytical data conform to the molecular formula $Sb(SR)_3$. All the relevant data are summarized in Table - I.

Infrared spectra of the products have been recorded on Perkin – Elmer spectrophotometer (RXI) in the region of 4000 – 450 cm^{-1} using potassium bromide pellets and the relevant data are summarized in Table-II.

Perusal of the infrared spectral data reveal[50] that there is no absorption band corresponding to ν(S – H) band, i.e., in the region of 2603 – 2499 cm^{-1} which supports the replacement of thiol proton by anodic antimony. However, characteristic bands are observed in the regions of 658 – 650 cm^{-1}, 530 – 523 cm^{-1} and 458 – 451 cm^{-1}.

Survey of literature[51-52] reveals that two bands appear in the region of 535 – 451 cm^{-1} due to ν(Sb – S) stretching vibrations. Terminal ν(Sb – S) bands appear in the region of 535 – 523 cm^{-1} and bridged ν(S – Sb – S) bands appear in the region of 462 – 451 cm^{-1}. In the light of this, the bands appearing in the regions of 530 – 523 cm^{-1} and 458 – 451 cm^{-1} in the infrared spectra of the present products can be assigned to ν(Sb – S) terminal and ν(S – Sb – S) bridged stretching vibrations respectively.

Literature reports[50-53] that the infrared bands due to ν(C – S) stretching vibrations appear in the region of 658 – 650 cm^{-1}. In the present products, the infrared basnds appearing in the region of 658 – 650 cm^{-1} can thus be assigned to ν(C – S) stretching vibrations.

Analytical data, absence of bands due to ν(S – H) stretching vibrations and presence of ν(Sb – S) and ν(C – S) stretching vibrations in the infrared spectra of the present products reveals that the protons of the thiol molecules are replaced by the sacrificial anodic antimony in the these electrochemical reactions. Thus the products of present electrochemical reactions can be characterized as antimony(III) thiolates.

Appearance of bridged ν(S – Sb – S) stretching vibrations, insoluble behavior of all these products in various organic solvents and high melting point of the products indicate that the present products may be polymeric in nature through thiolate bridging.

Current efficiencies of all these systems have also been determined and are listed in Table-I. Perusal of Table reveals that the current efficiencies of all these systems are quite high (0.83 – 0.97 g-eq F^{-1}). High current efficiencies of these systems show that the reaction leading to the formations of antimony(III) thiolates are the predominant reactions of these systems. The reaction scheme for these systems can be as given below:

At cathode:

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

At Sacrificial anode:

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

Table-I: Electrolysis Characteristics, Analytical and other Related Data of Electrolysis of Thiols 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	40	720	$Sb(SC_4H_{10})_3$	Light Brown	30.9 (31.07)	36.4 (36.75)	7.32 (7.65)	24.3 (24.50)	0.91
2-Methylpropane-2-thiol	60	720	$Sb(SC_4H_9)_3$	Light Brown	31.2 (31.31)	36.9 (37.04)	6.74 6.94)	24.1 (24.69)	0.83
Pentane-1-thiol	50	720	$Sb(SC_5H_{11})_3$	Light Brown	27.8 (28.26)	41.2 (41.78)	7.54 (7.66)	21.9 (22.28)	0.97
Propane-2-thiol	40	720	$Sb(SC_3H_8)_3$	Light Brown	34.25 (34.76)	30.24 (30.86)	6.23 (6.85)	27.16 (27.46)	0.89
Butane-1-thiol	40	720	$Sb(SC_4H_9)_3$	Light Brown	30.94 (31.27)	36.94 (37.02)	6.54 (6.93)	23.78 24.14	0.94

Table-II: Selected Infrared Absorption Bands of Products of Electrolysis of Various Thiols at Antimony Anode

System	Absorption band (cm^{-1})	Possible assignment
1-Methylpropane-1-thiol	458(s)	ν(S – Sb – S)
	530(s)	ν(Sb – S)
	650(s)	ν(C – S)
2-Methylpropane-2-thiol	451(s)	ν(S – Sb – S)
	528(s)	ν(Sb – S)
	658(s)	ν(C – S)
Pentane-1-thiol	458(s)	ν(S – Sb – S)
	523(s)	ν(Sb – S)
	656(s)	ν(C – S)
Propane-2-thiol	453(s)	ν(S – Sb – S)
	530(s)	ν(Sb – S)
	655(s)	ν(C – S)
Butane-1-thiol	455(s)	ν(S – Sb – S)
	530(s)	ν(Sb – S)
	658(s)	ν(C – S)

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 and organometallic compounds. Therefore, a variety of antimony compounds such thiolates compounds 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 and organoantimony compounds.

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