

ELECTROSYNTHESIS OF TARTARIC ACID FROM GLYOXYLIC ACID

S THANGAVELU

Central Electrochemical Research Institute, Karaikudi 623 006

ABSTRACT

Electrohydrodimerization of glyoxylic acid is studied in aqueous potassium chloride solution under different pH with silver and mercury cathodes using the controlled potential electrolysis technique. Identification, analysis and product isolation are carried out. In these experiments tartaric acid is found to be the major product along with some amount of glycollic acid.

Key words: Tartaric acid, electrosynthesis, glyoxylic acid

INTRODUCTION

Tartaric acid is a very useful natural product. It occurs in the juice of grapes and it is a byproduct in wine industry. It is used in textile printing, dyeing and pharmaceutical industries [1]. Industrially, tartaric acid is produced by the oxidation of carbohydrates and maleic acid [2] although there are other chemical methods involving a number of chemical steps [1].

It is reported that tartaric acid is one of the electrochemical reduction products of glyoxylic acid [3]. The above reduction has been studied mostly on dropping mercury electrode [4,5] and no detailed information is available about the formation of tartaric acid although the synthesis of tartaric acid by electrochemical method seems to be a very interesting one. In the present paper, the experimental results of the reduction of glyoxylic acid at controlled potential conditions which favour the formation of tartaric acid are reported.

EXPERIMENTAL

Controlled potential electrolysis

All laboratory scale experiments were carried out in a divided cell at controlled potentials. 175 ml of 1 M potassium chloride solution taken in a cylindrical vessel of 400 ml capacity was used as catholyte. 8-10% solution of potassium sulphate was used as anolyte and it was taken in a box type cation exchange membrane diaphragm. Silver sheet electrode (20 cm² immersed area) was used as cathode and lead plate was used as anode. 6-8 g of glyoxylic acid was added to the catholyte in the form of concentrated solution and the pH of the catholyte was adjusted to neutral and alkaline pH by the addition of potassium hydroxide solution. Catholyte was mechanically stirred by a glass stirrer using a fractional HP motor. The temperature of the electrolyte was maintained between 25° and 35° C by external cooling with a water bath.

In these experiments a potentiostatic three-electrode system was employed. The working electrode potential was maintained constant between -1.35 V and -1.45 V vs SCE and the reference electrode was connected to the working electrode through an agar agar potassium chloride filled capillary. Experiments were carried out at neutral and alkaline pH and the pH was maintained by the addition of small amounts of dilute hydrochloric acid during electrolysis. Electrolysis was continued up to 80-90% conversion of glyoxylic acid. Similar experiments were done with mercury pool cathode.

RESULTS AND DISCUSSION

Determination of the species

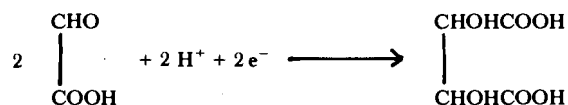
The solution obtained after electrolysis was analysed qualitatively for the

presence of tartaric acid and glycollic acid both by colour test as well as by paper chromatographic analysis [6, 7]. Quantitative analyses of tartaric acid [8], glycollic acid [8] and unreduced glyoxylic acid [9] were also carried out. Both qualitative and quantitative analyses of the electrolysed solution have confirmed the formation of tartaric acid.

Product isolation

The electrolysed solution was acidified to pH 3.2 to 3.5 by the addition of glacial acetic acid. The solution was stirred well and cooled. Potassium acid tartarate [10] of d,l-mixture whose solubility is very low when compared with the mesoform was precipitated out and the precipitate was collected and dried. The soluble portion of the meso form of tartaric acid was precipitated as calcium salt and the meso tartaric acid was regenerated by the addition of sulphuric acid solution. The filtrate obtained after the removal of calcium sulphate was concentrated to collect the crystallised meso tartaric acid.

Table I gives the results of the controlled potential experiments done at neutral and alkaline pH. Tartaric acid with a maximum of 72% yield was obtained along with 20-40% yield of glycollic acid. The above experimental results have confirmed that glyoxylic acid undergoes reductive dimerization as follows:



CONCLUSION

Tartaric acid can be prepared with good yields by electrohydrodimerization of glyoxylic acid at neutral and alkaline pH conditions using silver and mercury cathodes.

Acknowledgement: The author wishes to thank Dr H V K Udupa, ex-Director, Central Electrochemical Research Institute, Karaikudi for his keen interest and guidance in this work.

REFERENCES

1. I. L. Finar, Organic Chemistry, Vol. I, Longmans Green and Co., Ltd., (1951)
2. Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 13, John Wiley and Sons, New York (1978) p. 111
3. E. Bauer, Z *Elektrochem.*, **37** (1931) 255

Table 1: Product analysis of controlled potential electrolysis of glyoxylic acid

Expt. No.	pH	Electrode potential Volt vs. SCE	Amount of glyoxylic acid taken (g)	Total ampere hours passed	Unreduced glyoxylic acid present (g)	Tartaric acid estimated (g)	Yield of tartaric acid %	d,l mixture of tartaric acid (g)	Meso tartaric acid (g)	Glycollic acid (g)	Yield of glycollic acid %
Silver cathode											
1	7-8	-1.45	6.5	1.94	1.260	3.033	55.7	1.970	1.060	1.200	43.5
2	7-8	-1.40	6.5	1.67	1.55	3.360	71.7	2.380	0.980	0.655	27.6
3	12-1	-1.45	6.5	2.35	0.286	3.580	54.4	2.120	1.460	1.500	45.0
4	7-8	-1.40	7.5	1.83	2.170	3.590	69.9	2.310	1.285	0.736	28.3
Mercury pool cathode											
5	7-8	-1.40	5.5	1.90	0.260	3.270	61.5	2.130	1.140	1.020	37.9
6	7-8	-1.40	5.5	1.88	0.367	3.510	66.8	2.390	1.120	0.860	32.3

4. J Kúta, *Coll Czech Chem Commun*, **24** (1959) 2532

5. J Kúta, *Coll Czech Chem Commun*, **28** (1963) 1593

6. H Middleton, *Systematic Qualitative Organic Analysis*, Second Edition, reprinted (1952) p 73

7. F W Danison Jr and E F Phares, *Anal Chem*, **24** (1952) 1628

8. K K Sen Gupta and A K Chatterjee, *Indian J Chem*, **9** (1971) 497

9. P Thirunavukkarasu, K Jayaraman, S Thangavelu, P Subbiah, K S Udupa and H V K Udupa, *Symp Industr Oriented Basic Electrochem*, 2nd Madras, Dec. 9-13 (1980)

10. R E Kirk and D F Othmer (Ed) *Encyclopedia of Chemical Technology*, Interscience Publication, New York, 13 (1954) p 645