

## ELECTROSYNTHESIS OF TARTARIC ACID FROM MALEIC AND FUMARIC ACIDS

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Tartaric acid has been electrochemically synthesised by hydroxylating the olefinic double bond of maleic and fumaric acids through epoxidation and hydrolysis. Epoxidation of these olefinic compounds has been electrochemically achieved using in situ regeneration of redox reagents containing suitable catalysts. Effect of various experimental parameters on the epoxidation, such as current density, pH, temperature, concentration of the reactant, concentration of the catalyst and nature of the supporting electrolyte-cum-reactant has been studied. Conditions for the conversion of the corresponding epoxides formed into tartaric acid have been standardised.

**Key Words:** Epoxidation, tartaric acid

## INTRODUCTION

Tartaric acid is used in textile printing, dyeing and pharmaceutical industries [1,2]. It is also used in the preparation of effervescing drinks, baking powder, fruit jellies and in the manufacture of artificial wine [2].

Tartaric acid is obtained as a byproduct in wine industry [1,3]. Industrially, tartaric acid is produced by the oxidation of carbohydrates and maleic acid [2]. Earlier many methods have been tried for the oxidation of carbohydrates, maleic and fumaric acids, using different oxidizing agents. Carbohydrates have been oxidized by nitric acid [4] in presence of vanadate catalyst. Bacterial fermentation of glucose to tartaric acid is also reported [5]. A detailed study of the oxidation of maleic and fumaric acids [4] has been made using a number of oxidizing agents like dilute alkaline potassium permanganate [6], nitric acid [7], gaseous oxygen in the presence of a catalyst [8,9], hypochlorous acid and hydrogen peroxide [4,10-14]. It is reported that oxidation with  $\text{KMnO}_4$  and nitric acid gives tartaric acid as one of the oxidation products directly with low yield. But oxidation with  $\text{H}_2\text{O}_2$  and  $\text{HOCl}$  gives tartaric acid through the formation of epoxysuccinic acid as intermediate. Recently electrochemical hydrodimerization of glyoxylic acid to tartaric acid has been reported [15].

At present tartaric acid is obtained synthetically by treatment of maleic acid with  $\text{H}_2\text{O}_2$  in the presence of a catalyst and this process has reached the commercial stage [16]. This process involves the addition of 60%  $\text{H}_2\text{O}_2$  to 40% aqueous maleic acid in the presence of a transition metal salt as catalyst. The epoxysuccinic acid which is formed as an intermediate is hydrolysed by boiling and tartaric acid is isolated from the solution.

In this paper the results of the study on the electro-oxidation of maleic and fumaric acids into tartaric acid in presence of sodium bromide have been reported. Tartaric acid is obtained through the formation of haloohydrin and epoxide and both the electrode reactions are being utilised to get the epoxide within the cell. The epoxide is hydrolysed by boiling with alkali to get tartaric acid.

## EXPERIMENTAL

## Cell set up

The cell consisted of one litre beaker cut to a height of 18 cm and fitted with a wooden cover, having necessary openings for the introduction of the rotating cylindrical graphite anode and two stationary graphite plates as cathodes kept on both sides of the anode, thermometer and for feeding or removal of electrolyte. A graphite rod of 2.5cm diameter was fitted to a 30 (1) x 1 cm (dia) copper rod and attached to the lower end of the shaft of a fractional H.P. motor. The electrical contact was given through mercury taken in a mercury cup attached to the top end of the shaft. The speed of rotation of the electrode was kept at 1000 rpm. The electrolyte (500 ml) was sodium or potassium salt of maleic and fumaric acids (30-40 g/l) to which sodium bromide/sodium chloride was also added for generating hypohalite through oxidation of halide ion. The temperature of the cell was maintained at the desired level by a water bath with an electrical heating arrangement. Required amount of current was passed under different experimental conditions.

## Product isolation

After the electrolysis, the solution was made alkaline by the addition of 15g of KOH and hydrolysed by boiling for one hour. Tartaric acid content was estimated using ceric sulphate solution [17]. Potassium acid tartrate was isolated by acidifying the solution to pH 3.2 - 3.5 using HCl. The tartaric acid content of the filtrate was estimated and isolated as calcium tartrate.

## RESULTS AND DISCUSSION

Table I shows the effect of temperature, catalyst concentration and alkali halide on the current efficiency and yield of the product at a current density of 0.4  $\text{kA.m}^{-2}$ .

The current efficiency was found to increase with increase in temperature upto 318K. Above 323K the current efficiency and yield of product decreased. Catalyst concentration above 1 g/l for the reactant concentration of 30 - 40 g/l has almost no effect on current efficiency. The increase of the concentration of sodium

TABLE-I: Electrolysis conditions for the epoxidation of maleic acid and fumaric acid in presence of NaBr/NaCl

Electrolyte volume: 500 ml; Cathode: Graphite plate; Anode: Rotating cylindrical graphite rod; Current density: 0.4 kA.m<sup>-2</sup>; pH 6 - 8

Expt. No.	Maleic acid taken (g)	Fumaric acid taken (g)	NaBr (g)	Catalyst (g)	Temp (K)	Tartaric acid estimated (g)	Current efficiency %	Yield (estimated %)
1.	20	-	5	0.5	308 -313	18.3	71	71
2.	20	-	5	0.5	308 -313	16.7	65	65
3.	20	-	5	0.4	303 -308	19.1	74	74
4.	-	15	5	0.5	308-313	9.4	70	68
5.	-	15	5	0.5	313-323	9.5	77	64
6.	-	20	5	1.0	313-323	12.7	79	64
7.	-	20	10	0.5	303-308	13.1	64	80
8.	-	20	10	0.5	313-318	19.5	86	88
9.	-	20	10	0.5	318-323	16.3	78	81
10.	-	20	10	0.5	313-318	15.2	74	80
(0.6 kA.m <sup>-2</sup> )								
11.	-	20	10	0.5	313-318	17.5	81	85
12.	-	15	10	1.0	313-318	-	28	-

(NaCl)

bromide has increased the current efficiency and yield. The use of sodium chloride has decreased the current efficiency.

It has been observed that the pH of the electrolyte is self maintained and this gives an indirect indication that epoxide is the electrolysis product.

## REFERENCES

1. *Thorpe's Dictionary of Applied Chemistry*, Vol. XI, Fourth Edition, Longmans 1954 p 422
2. Kirk-Othmer, *Encyclopedia of Che. Tech. Vol. 13*, Third Edition, A Wiley- Interscience, Publication (1981) p 113
3. G M Dyson, *Chem Age (London)*, 20 (1929) 331
4. J M Church and R Blumberg, *Ind Eng Chem*, 43 (1951) 1780
5. J Kamlet, U S Pat. 2314831 (March 1943)
6. S Tanatar, *Ber*; 12 (1879) 2293; *Ber*; 13 (1880) 1383
7. R A Hales, U S Pat. 2 419019 and 2419020 (April 1947)
8. R Pasternack and E V Brown, U S Pat. 2197021 (April 1940)
9. W E Barch, U S Pat. 2417230 (Mar, 1947)
10. D F Lewis and A B Rodriguez, Brit. Pat. 1,442748 (July 1976)
11. N Kazutani and coworkers, Nippon Peroxide Co. Ltd., Japan Kokai 7785 119 (July 1977)
12. M Kataoka, K Kosoi and M Ono, Japan Kokai 76,113,822 (Oct 1976)
13. K Petrisich, P Korl and F Pogotiach, Ger. Offen 2,555699 (July 1976)
14. G Prescher and G Schreyer, Ger. Offen 2,543,333 (May 1977)
15. S Thangavelu Ph.D. Thesis, Madurai Kamaraj University Madurai (1985), *B Electrochem*, 1 (1985) 553
16. J A Bewsey, *Chem Ind (London)*, 3 (1977) 119
17. K K Sengupta and A K Chatterjee, *Indian J Chem*, 9 (1971) 497