

PREPARATION OF TARTARIC ACID

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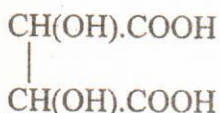
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ABSTRACT

The present investigation is concerned with the preparation of dl-tartaric acid by epoxidation of maleic acid with hydrogen peroxide using sodium tungstate as a catalyst followed by hydrolysis of resulting cis-epoxysuccinic acid. The operating conditions of the reaction were studied in detail. The most favorable operating conditions were reactant molar ratio of maleic acid to hydrogen peroxide of 1.5, catalyst ratio (weight percent of catalyst to maleic anhydride) of 10, temperature of 70 °C and initial concentration of hydrogen peroxide in aqueous solution of the reaction of 10%.

INTRODUCTION

Tartaric acid (2,3-dihydroxy butanedioic acid 2,3-dihydroxy succinic acid), $C_4H_6O_6$, containing two hydroxyl and two carboxyl groups attached to an ethane hydrocarbon structure, possesses two centers of asymmetry.



Tartaric acid is used in the production of food and drugs. It exists in four modifications namely, dextro-tartaric acid and levo-tartaric acid, which exhibit optical activity, and racemic (dl-tartaric) acid and meso-tartaric acid which are optically inactive^(1,2).

Dextro-tartaric acid and levo-tartaric acid have the same physical properties except for their effect on plane-polarized light, specific rotation $[\alpha]_D^{25}$, and bearing the mirror-object relationship to each other.

Racemic acid is a molecular compound, all its crystal contain equal numbers of molecules of the d and l isomers. It is optically inactive and can be separated into the active forms.

Meso-tartaric acid has no effect upon the plane of polarization of plane-polarized light. It is optically inactive and can not be separated into the two active forms.

The main commercial product in the world is the natural, dextrorotatory form, (R-R*, R*)- tartaric acid, [L(+)-tartaric acid]. This enantiomer occurs in grapes

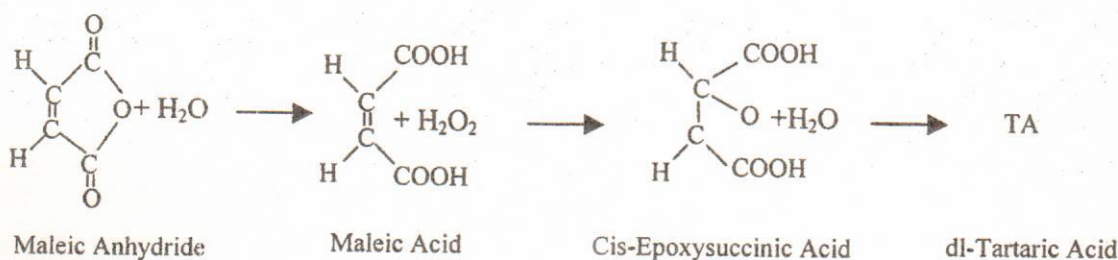
as its acid potassium salt (cream of tartar, potassium hydrogen tartarate, potassium bitartarate), $KHC_4H_4O_6$. In the fermentation of grape juice to wine, this salt deposits in the fermentation vessels. The free crystallized tartaric acid was first obtained from such fermentation residues by Scheele in 1769, and even today this continues to be the chief source of industrial acid.

L(+)-tartaric acid is produced commercially by conversion of the crude cream of tartar to calcium tartarate which is decomposed with dilute sulfuric acid to tartaric acid and calcium sulfate.

In Europe, South Africa, and Japan, racemic (R*,R*)- tartaric acid (dl- tartaric acid) is also produced commercially. It is obtained synthetically by treatment of maleic acid or its anhydride with hydrogen peroxide in the presence of a catalyst, e.g., tungstic acid⁽³⁻⁹⁾.

The present work is concerned with preparation of synthetic dl- tartaric (racemic) acid by hydroxylation of maleic anhydride. The major cost in this production is the two raw materials, hydrogen peroxide and maleic anhydride. Hydrogen peroxide has had a history of good stability on prices and availability. Maleic anhydride can be produced in Iraq by oxidation of n-butane, the basic and detailed design of this project is available in the Ministry of Industry.

The chemical reaction for the production of dl-tartaric acid is represented by:



EXPERIMENTAL

Materials

Maleic Anhydride ($C_4H_2O_3$)

Maleic anhydride manufactured by (Riedel-de Hean AG) with a purity of 99.5% was used for preparation of (R*, R*)-tartaric acid. The molecular weight of maleic anhydride is 98.06 g/gmole and melting point is 52.9 °C.

Hydrogen Peroxide (H_2O_2)

Technical hydrogen peroxide with concentration of 47 wt% was used in the epoxidation of maleic acid. The molecular weight of hydrogen peroxide is 34.016 g/gmole.

Catalysts

Sodium Tungstate Dihydrate ($Na_2WO_4 \cdot 2H_2O$)

Sodium tungstate dihydrate manufactured by (May and Baker LTD.) with a purity of 99% was used to catalyze epoxidation of maleic acid. The molecular weight of sodium tungstate dihydrate is 329.86 g/gmole.

Sodium Molybdate Dihydrate ($Na_2MoO_4 \cdot 2H_2O$)

Sodium molybdate dihydrate manufactured by (Merck) with a purity of 99% was used to catalyze epoxidation of maleic acid. The molecular weight of sodium molybdate dihydrate is 241.95 g/gmole.

Procedure

Figure (1) shows a schematic diagram of laboratory experimental unit used in this work. The required quantity of maleic anhydride was added to the aqueous solution of sodium tungstate or molybdate catalyst and the solution was then heated to 50-55 °C to dissolve all the maleic anhydride added. Then the solution was filtered to remove any solid impurities, and then charged through the dropping funnel into the reaction flask. A measured quantity of 47% hydrogen peroxide was added to the stirred mixture. The desired temperature was maintained for a specified length of time by using a hot water bath. It was found advantageous to use stirrer speeds lower than 120 rpm to avoid unnecessary loss of oxygen. The reaction was considered complete with the presence of hydrogen peroxide could no longer be detected in the solution by using starch potassium iodide paper. At the end of the reaction, the temperature was slowly increased and the reaction mixture was brought to reflux temperature of 102 °C for about 1 hour to complete hydrolysis of the intermediate epoxy compound for the formation of tartaric acid. After that, tartaric acid and unreacted maleic acid were determined by using a suitable analytical methods.

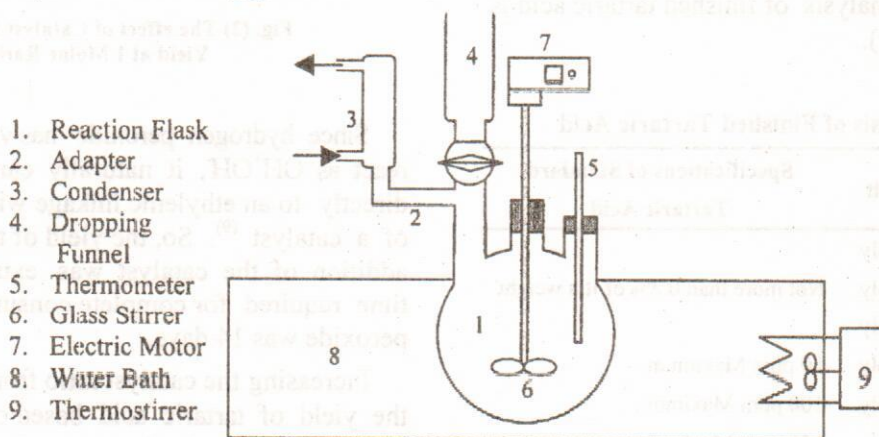


Fig. (1) Laboratory Experimental Unit

Methods of Analysis

Identification of Tartaric Acid

After complete hydrolysis of the intermediate epoxy compound in the product, the resulting solution was cooled to 0 °C with stirring, and after about 5 minutes tartaric acid was crystallized. For complete crystallization, the solution was held at 0 °C for 6 hours. The crystals were separated from mother liquor by filtration and dried at 110 °C. These crystals were identified for tartaric acid-resorcinol solution detection method⁽¹¹⁾, melting point⁽¹²⁾ and infrared adsorption spectra⁽¹²⁾.

Quantitative Determination of Tartaric Acid

Tartaric acid was determined quantitatively by adapting the method which is commonly used in analysis of wine less and argols⁽⁵⁾. This method depends upon the conversion of the tartaric acid to the acid potassium salt and subsequent titration with standard alkali^(10,11).

Quantitative Determination of Unreacted Maleic Acid

Unreacted maleic acid was precipitated as the barium maleate monohydrate according to the method of Milas and Walsh⁽¹³⁾, as follows:

After separation of (R*, R*)-tartaric (racemic) acid from the sample as potassium acid tartrate, 10 ml was taken from the filtrate and a slight excess of the equivalent amount of solid barium chloride was added. The resulting solution was made alkaline to litmus with concentrated ammonium hydroxide, diluted to three times its volume with 95% alcohol and the precipitate was collected, dried at 110 °C and weighed as barium maleate monohydrate (C₄H₂O₄Ba.H₂O).

Analysis of Finished Tartaric Acid

Tartaric acid produced was recrystallized from water, filtered, and dried at 110 °C. Then the purity (assay) of the dried crystals was determined by using the following procedure:

0.65 g of dried crystals was dissolved in 25 ml of water and titrated with 1 M sodium hydroxide volumetric solution to the first pink color using 0.5 ml of phenolphthalein solution as indicator.

$$\text{Assay} = \frac{\text{Weight percent of tartaric acid (C}_4\text{H}_6\text{O}_6)}{\text{Percent in the dried crystals}} =$$

$$= V * 0.07505 * 100 / 0.65$$

V = Volume of 1 M Sodium Hydroxide.

Assay of pure tartaric acid must be between (99.5-101%). Complete analysis of finished tartaric acid is presented in Table (1).

Table (1) Analysis of Finished Tartaric Acid

Type of Analysis	Result	Specifications of Standard Tartaric Acid
Identification	Comply	
Loss of drying	Comply	Not more than 0.2% of it's weight
Clarity	Comply	
Heavy metals	Comply	10 ppm Maximum
Chloride	Comply	100 ppm Maximum
Sulphate	Comply	150 ppm Maximum
Sulphated ash	Comply	Not more than 0.1%
Assay	100.5%	(99.5-101)%

Results and Discussion

Effect of Catalyst

The effect of catalyst ratio of the weight of sodium tungstate dihydrate to the weight of malic anhydride, upon the yield of tartaric acid is shown in Figure (2).

From this figure it is shown that in the absence of catalyst, the yield of tartaric acid was extremely low. A marked increase in yield was obtained when the reaction was carried out in the presence of a trace of sodium tungstate catalyst.

This figure also shows that the yield of tartaric acid based on malic anhydride (weight percent of

tartaric acid produced to malic anhydride used in the reaction) and the yield of tartaric acid based on hydrogen peroxide (weight percent of hydrogen peroxide converted to tartaric acid to hydrogen peroxide used in the reaction) increase very rapidly with increase in catalyst ratio (weight percent of sodium tungstate dihydrate catalyst to malic anhydride used in the reaction) up to 0.4, after which further additions of catalyst increase the yield slowly.

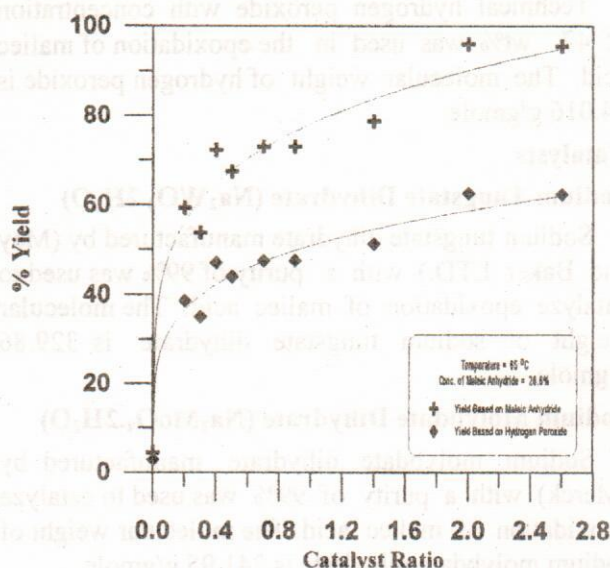


Fig. (2) The effect of Catalyst Ratio on Tartaric Acid Yield at 1 Molar Ratio of Reactants

Since hydrogen peroxide has very little tendency to react as OH⁺OH⁻, it naturally can not readily added directly to an ethylenic linkage without the mediation of a catalyst⁽⁹⁾. So, the yield of tartaric acid without addition of the catalyst was extremely low, and the time required for complete consumption of hydrogen peroxide was 14 days.

Increasing the catalyst ratio from 0 to 0.4 increases the yield of tartaric acid based on malic anhydride very rapidly and decreases the time required for complete consumption of hydrogen peroxide (from 14 days to 20 hours) due to the action of the sodium tungstate catalyst. The catalyst react with hydrogen peroxide to form higher unstable pertungstic acid⁽¹⁵⁾, which then reacts with malic acid to form cis-epoxysuccinic acid. Then epoxysuccinic acid is converted to tartaric acid by hydrolysis at reflux temperature.

Molybdic acid forms compounds of the per acid type with hydrogen peroxide and gives results similar to that obtained with tungstic acid. One experiment was carried out using sodium molybdate catalyst and the following operating conditions: reactant ratio was 1.5, catalyst ratio was 0.8 and initial concentration of maleic anhydride in aqueous solution was 27% at temperature of 65 °C. The yield of tartaric acid based

on maleic anhydride was 51.91% and the time required to complete the reaction was 16 hours, while, the yield based on maleic anhydride under the same conditions using sodium tungstate catalyst was 59.11% and the time required to complete the reaction was 10 hours.

Effect of Molar Ratio of Reactants

Figure (3) shows the effect of reactant ratio on the yield based on hydrogen peroxide using catalyst ratio of 10. From this figure, it is clear that excess hydrogen peroxide over the stoichiometric amount has little effect upon the conversion of maleic anhydride, but an excess of maleic acid increases the yield of tartaric acid based on hydrogen peroxide considerably. The yield of tartaric acid based on hydrogen peroxide increases steadily with increase in the reactant ratio of maleic acid to hydrogen peroxide up to 1.5, but further amounts of acid have only a small effect on the yield. On the other hand, the yield based on maleic anhydride decreases rapidly with increase in reactant ratio from 1 to 2. For optimum conditions a 50% excess of maleic acid is therefore recommended.

Results similar to that given in Figure (3) are also obtained by Church and Blumberg⁽⁵⁾ Bewsey⁽⁴⁾ obtained 84% yield based on hydrogen peroxide using

reactant ratio of 1.2 and a molybdenum catalyst, while, in the present work, the yield based on hydrogen peroxide was 84% using reactant ratio of 1.5 and sodium tungstate dihydrate catalyst ratio of 10.

Effect of Temperature

Table (2) shows the effect of temperature on the tartaric acid yields using reactant ratio of reactants of 1.5 and catalyst ratios of 1 and 10.

For the catalyst ratio of 1, the temperature has little effect upon the tartaric acid yields. But for catalyst ratio of 10 the yield of tartaric acid decreased rapidly as the temperature increased from 70 to 110°C.

Table (2) also shows that the time required for complete consumption of hydrogen peroxide (time of reaction) is decreased as the temperature of the reaction is increased (see Figure 4).

These results show that the best temperature is 70°C.

At temperatures higher than 70 °C and at high catalyst ratio, the yield of tartaric acid are decrease due to the losses of oxygen by decomposition of pertungstic acid to oxygen and tungstic acid as it was observed by English and Gregory⁽¹⁶⁾ for performic acid.

Table (2) Effect of Temperature at 1.5 Reactant Ratio

Conditions: conc. of H₂O₂ = 10%; Maleic anhydride = 3.5 gmole/liter

Exp.No	Temp. °C	Catalyst Ratio =1			Catalyst Ratio =10	
		% Yield Based on Maleic Anhydride	% Yield Based on Hydrogen Peroxide	Time of Reaction (h)	% Yield Based on Maleic Anhydride	% Yield Based on Hydrogen Peroxide
1	38	63.80	61.62	45	-	-
2	50	62.16	59.40	20	-	-
3	70	59.00	57.30	7	86.02	84.30
4	87	58.90	55.13	3	-	-
5	110	61.20	58.60	1	57.60	56.45

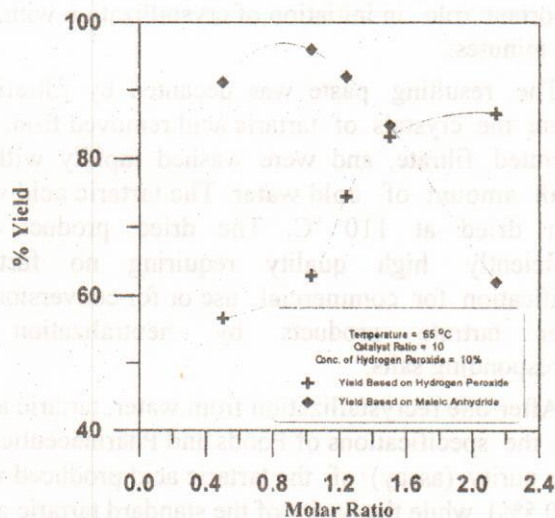


Fig. (3) The effect of Molar Ratio of Reactants on Yields of Tartaric Acid

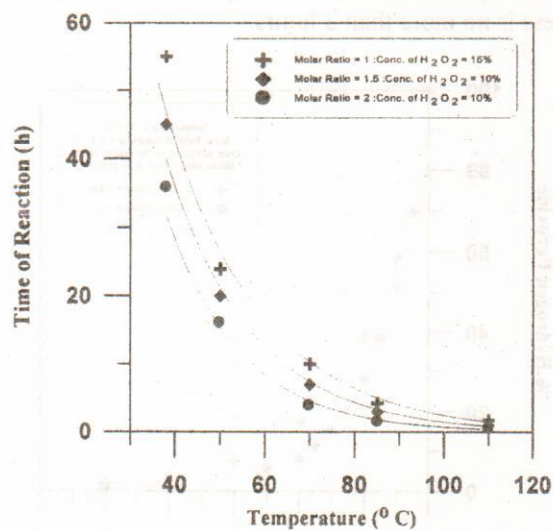


Fig. (4) The effect of Temperature on Time Required for Complete consumption of Hydrogen Peroxide Catalyst Ratio 1%

This temperature is within the range of 60-80 °C given by Church and Blumbey⁽⁵⁾. Mugdan and Young⁽⁹⁾ stated that the optimum temperature is located between 60-70 °C, below this similar yields are obtained but at higher time of reaction.

Effect of Initial Concentrations of Reactants

Table (3) shows the effect of initial concentrations of the reactants on tartaric acid yield using molar ratio of reactants of 1 catalyst ratio of 1% at 70 °C. The initial concentrations of hydrogen peroxide used were 5, 10, 15, and 21.5%.

Changes in the initial concentrations of the reactants have only a small effect upon the yield of tartaric acid.

For hydrogen peroxide concentrations of 15 and 21.5%, the reaction was very vigorous due to the exothermic nature of the reaction and it was difficult to adjust the temperature at 70 °C. The temperature of the reaction was more controllable using hydrogen peroxide concentrations of 10% and lower. For hydrogen peroxide concentrations lower than 10%, the quantities of tartaric acid produced by crystallization after the end of the reaction were less than that obtained when the hydrogen peroxide concentration was 10% and higher due to the presence of higher quantities of water.

From these results, concentration of 10% of hydrogen peroxide in the aqueous solution of the reaction is therefore recommended.

Table (3) Effect of Concentrations of Hydrogen Peroxide and Maleic Anhydride on Tartaric Acid Yield
Conditions: Temp.= 70 °C; Reactant Ratio =1; Catalyst Ratio =1

Exp. No.	Concentration of Reactants		% Yield Based on Maleic Anhydride
	Hydrogen Peroxide (C ₂) (wt%)	Maleic Anhydride (g. mole/liter) of Solution	
1	21.5	4.60	75.6
2	15	3.50	78.2
3	10	2.50	76.4
4	5	1.35	72.8

Rate of Consumption of Hydrogen Peroxide

Following the course of the reaction by the rate of consumption of hydrogen peroxide, it is evident from Figure (5) that the major part of the reaction takes place rapidly, where more than 90% of hydrogen peroxide is consumed within the first 3 hours. There is some tendency for increasing the rate of hydrogen peroxide consumption with increasing the catalyst ratio. It seems that the optimum economical experimental time for this process is no more than 3 hours.

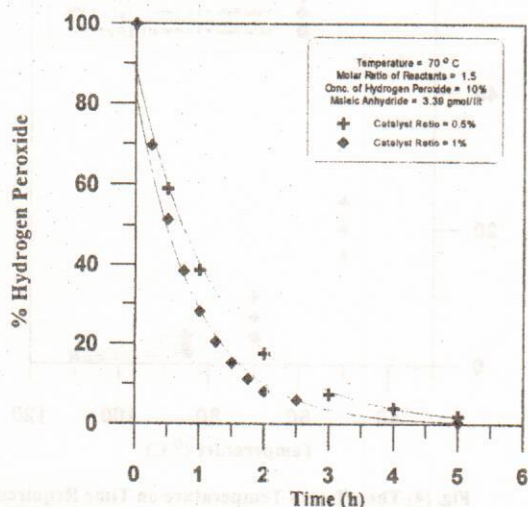


Fig. (5) Rate of Consumption of Hydrogen Peroxide
Catalyst Ratio 1%

Product Treatment

After hydroxylation of maleic acid by hydrogen peroxide, the product was cooled and then chilled to temperature of about 0 °C with vigorous mixing. Within a few minutes crystallization of tartaric acid commenced and was completed over a period of 6 hours. It was observed that vigorous stirring plays an important role in initiation of crystallization within a few minutes.

The resulting paste was decanted by filtration, where the crystals of tartaric acid removed from the saturated filtrate, and were washed rapidly with a small amount of cold water. The tartaric acid was then dried at 110 °C. The dried product was sufficiently high quality requiring no further purification for commercial use or for conversion to other tartrate products by neutralization to corresponding salts.

After one recrystallization from water, tartaric acid met the specifications of Foods and Pharmaceuticals. The purity (assay) of the tartaric acid produced was (100.5%), while the purity of the standard tartaric acid used in pharmaceuis (99.5-101%) (see Table 1). The saturated filtrate, containing some dissolved tartaric acid, catalyst, and unreacted maleic acid was reused in the next experiment. The catalyst, which was in the form of a soluble tungstic acid complex⁽¹⁵⁾, retains its

activity, and may be reused several times before renewal is necessary. Four experiments were carried out to show the possibility of reusing of catalyst without addition of fresh catalyst. Table (4) shows the results of these experiments using molar ratio of reactants of 1.5 and catalyst ratio of 10% at temperature of 70 °C. Tartaric acid yields based on hydrogen peroxide for the first, second, third, and fourth experiment were 84.3, 80.2, 82.4, and 79.56 respectively.

After several experiments, it is advisable to recover the soluble catalyst for reactivation by precipitation using hydrochloric acid^(5,15).

Hydrochloric acid of specific gravity 1.19 was added, dropwise, to the stirred filtrate containing 31-38 g of sodium tungstate dihydrate per liter. White precipitate of tungstic acid was precipitated and then filtered and dried at 70 °C. The addition of hydrochloric acid must be added dropwise because the white crystals of tungstic acid, which precipitated, were redissolved on continuing the addition of hydrochloric acid.

Table (4) Reusing of Sodium Tungstate Catalyst
Conditions: Temp.= 70 °C; Molar Ratio = 1.5; Catalyst Ratio = 10%

Exp. No.	% Yield Based on Hydrogen Peroxide
1	84.3
2	80.2
3	82.4
4	79.56

Conclusions

1. The recommended optimum conditions for preparation of tartaric acid are: reactant ratio of maleic anhydride to hydrogen peroxide of 1.5, catalyst ratio of 10, concentration of hydrogen peroxide in aqueous solution of 10%, and temperature of 70 °C.
2. DL- tartaric (racemic) acid produced from hydroxylation of maleic anhydride meets the specifications of Foods and Pharmaceuticals with purity (assay) of 99.7%.

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