

B.SC PART II PAPER ORGANIC

SUBSIDIARY

TOPIC:- Oxalic Acid, Citric Acid, Tartaric Acid

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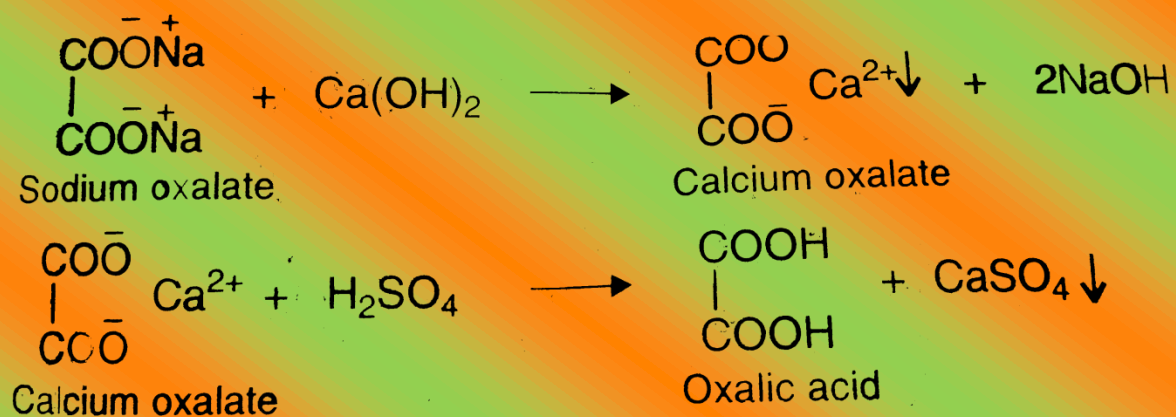
OXALIC ACID, ETHANEDIOIC ACID, HCOOH-COOH

It occurs as potassium hydrogen oxalate in the wood sorrel, rhubarb, and tomatoes. The insoluble calcium oxalate is found in some stony deposits in kidneys and bladder in human body.

Preparation. (1) Manufacture. Oxalic acid is made industrially by heating sodium formate to 400°C

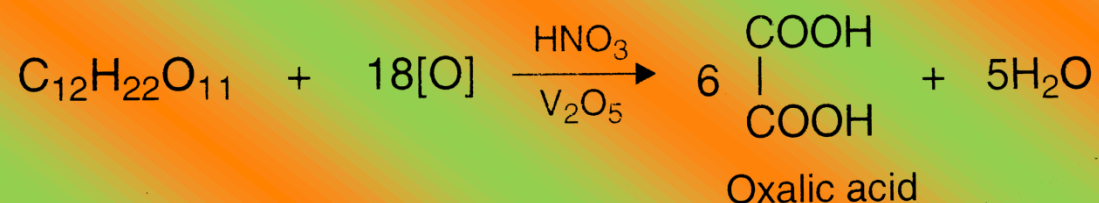


The sodium oxalate thus formed is dissolved in water and calcium hydroxide added to precipitate calcium oxalate. The solution is filtered and the filtrate treated with calculated quantity of dilute sulfuric acid to liberate the oxalic acid.



Calcium sulfate precipitates, and oxalic acid is crystallized from the filtrate as the hydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$.

(2) Laboratory Method. In the laboratory, oxalic acid made by oxidation of sucrose or molasses with concentrated nitric acid in the presence of vanadium pentoxide as catalyst.

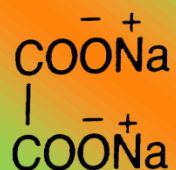


The –CHOH.CHOH- units present in sucrose molecule are split out and oxidized to oxalic acid properties. (physical). When crystallized from water, colorless prismatic crystals of oxalic acid hydrate, $(COOH)_2 \cdot 2H_2O$, are obtained. The hydrate melts at 101.5°C , while the anhydrous acid melts at 189.5°C . The hydrated acid becomes anhydrous when carefully heated to 150°C . Oxalic acid is an active poison, depressing the central nervous system and causing malfunction of kidneys.

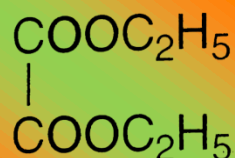
(Chemical)- Oxalic acid molecule is made of two carboxyl groups in direct union. It gives all the usual reactions of COOH group twice. Also, the acid gives some

peculiar reactions which involve the cleavage of the weakened linkage between the two highly oxidized carbon atoms.

- (1) **Formation of Mono- and Di-derivatives**- Oxalic acid is a much stronger acid than acetic acid and readily forms two series of salts, esters, acid halides and amides.



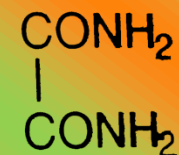
Disodium
oxalate



Diethyl
oxalate

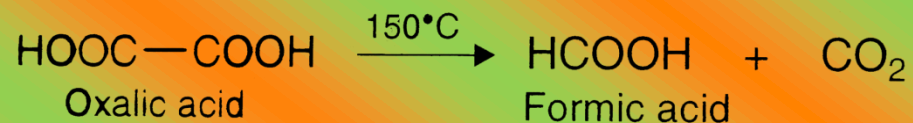


Oxalyl
chloride



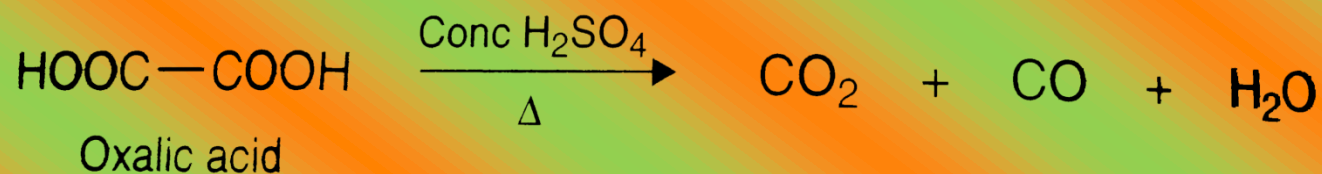
Oxamide

- (2) **Action of Heat**- When heated at 150°C, it decarboxylates to give formic acid.



(3) Action with Glycerol- Oxalic acid reacts with glycerol to form formic acid or allyl alcohol, depending upon experimental condition.

(4) Action with H_2SO_4 - When heated with concentrated sulfuric acid, it is decomposed to give carbon dioxide, carbon monoxide and water.



Uses- Oxalic acid is used:

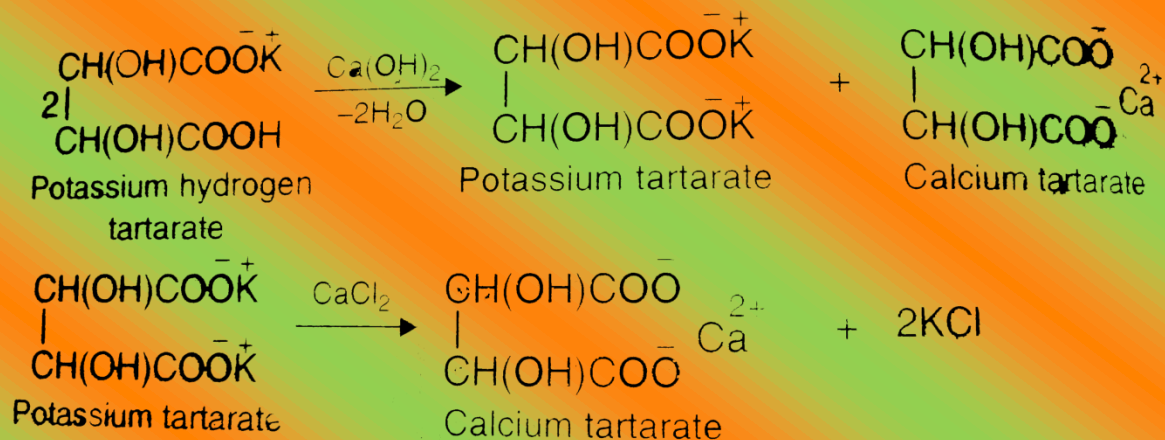
- (1) For removing ink stains and for bleaching straw for hats, since it reduces brown ferric compounds to soluble and almost colorless ferrous salts;
- (2) As a mordant in dyeing and calico printing;
- (3) In manufacture of inks and metal polishes;
- (4) For preparing allyl alcohol and formic acid in the laboratory;
- (5) In Redox Titrations.

TARTARIC ACID, 2,3-DIHYDROXYSUCCINIC ACID

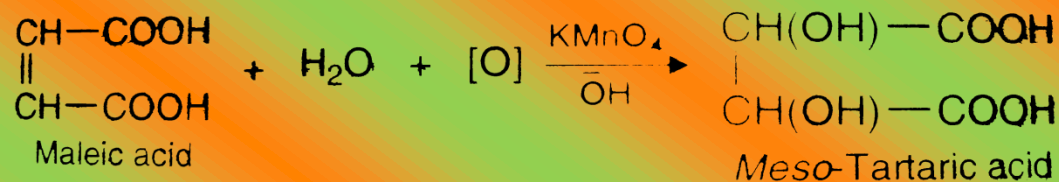
Tartaric acid occurs free and as potassium hydrogen tartarate in grape juice.

Preparation-

(1) **From Grape Juice-** Argol which is potassium hydrogen tartarate (cream of tartar), is formed as a sludgy precipitate during the fermentation of grape juice in wine making. It is dissolved in boiling water and neutralized with milk of lime. Calcium tartarate is precipitated, while potassium tartarate remains in solution. The calcium tartarate is separated by filtration and the filtrate treated with calcium chloride when potassium tartarate is also precipitated as calcium tartarate.



(2) **From Maleic Acid**- Maleic acid produced industrially by oxidation of cyclohexane is treated with alkaline KMnO_4 to get meso-tartaric acid.



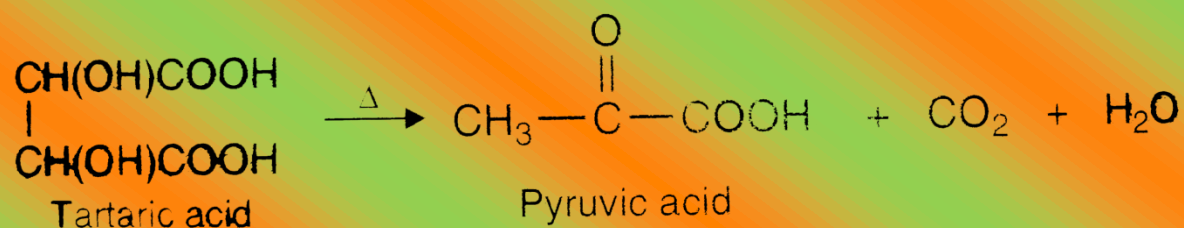
Properties- (physical)-Tartaric acid is a white crystalline substance, mp 171°C , having acidic taste. It is soluble in water and alcohol, but sparingly soluble in ether. Since it has two asymmetric carbon atoms, tartaric acid shows optical isomerism. The natural tartaric acid is the dextro variety, $\alpha = +12.7$.

(chemical)- Tartaric acid molecule has two secondary alcohol groups ($>\text{CHOH}$) and two $-\text{COOH}$ groups, and behaves accordingly.

(1) **Formation of Salts**- It forms two series of salts when treated with alkalis.



(2) **Action of Heat**- When heated, tartaric acid is converted to pyruvic acid.



Uses- (Tartaric acid is used:)

- (1) In carbonated beverages and effervescent tablets;
- (2) In baking powder;
- (3) As mordant;

- (4) In silvering of mirrors;
- (5) In tanning;

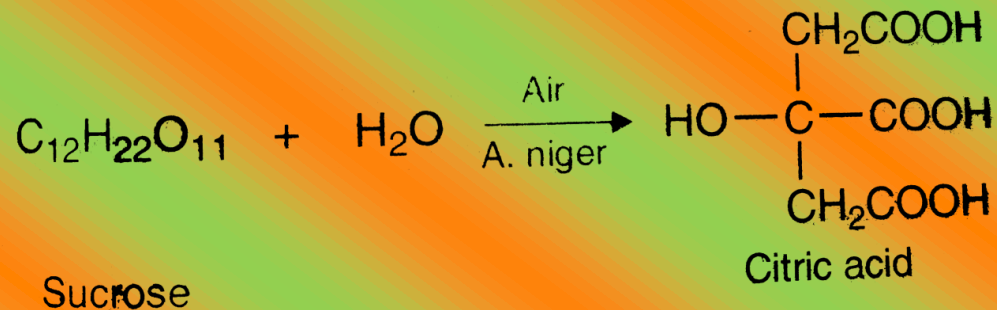
- (6) For preparing tartar emetic, cream of tartar, Rochelle salt etc.

CITRIC ACID, 2-HYDROXYPROPANE-1,2,3-TRICARBOXYLIC ACID

It occurs in the juice of citrus fruits such as lemons, limes, galgals and oranges.
Lemon juice contains 7-10 percent citric acid

Preparation:-

- (1) **From Molasses** – Molasses containing sucrose is diluted with water and subjected to fermentation with a microorganism *Aspergillus niger*.



The fermentation process is carried for 7 to 10 days at 26-28°C. The resulting solution of citric acid is neutralized with $\text{Ca}(\text{OH})_2$ to form insoluble citrate. This is washed with water and decomposed with dilute sulfuric acid. The calcium sulfate is filtered off and the solution concentrated under vacuum to get crystals of citric acid

- (2) **From Petroleum**- Recently it has been shown that certain strains of *Candida* (a yeast) can produce citric acid from n-alkanes derived from petroleum. This method when developed will revolutionize the citric acid industry.

USES:-

- (1) As acidulant in carbonated soft drinks, jams, jellies, candies, etc.

- (2) As medicinal in form of effervescent salts, magnesium citrate, a laxative;
- (3) As mordant;
- (4) As ferric ammonium citrate in the preparation of blueprint papers;

Thank You