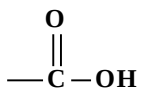
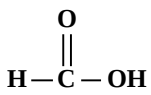
Identification of Carboxylic Acids

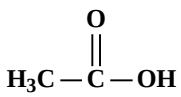
Carboxylic acids are organic compounds that have a carboxyl group attached to an alkyl group(RCOOH) or to an aryl group (ArCOOH). The 'R' may be a hydrogen and the result is formic acid. They may be mono carboxylated, multi carboxylated, substituted (*e. g.*, hydroxyl groups), or they may be aromatic



carboxyl group

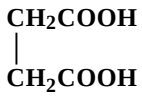


formic acid

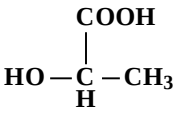


acetic acid

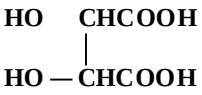
oxalic acid



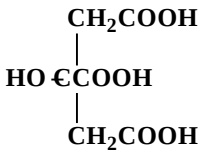
succinic acid



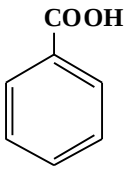
lactic acid



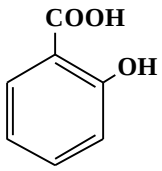
tartaric acid



citric acid



benzoic acid

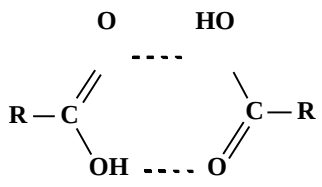


salicylic acid

Physical properties

- Only formic acid, acetic acid, and lactic acid are liquids at room temperature. The others are solids.
- Low molecular weight carboxylic acids are soluble in water and, therefore, lie under class S_1. Water insoluble acids dissolve in both sodium hydroxide solution and sodium bicarbonate solution, being classified under class A_1. When they react with sodium bicarbonate, they evolve carbon dioxide gas. This is considered as a good simple indication of them.

- Their boiling points are generally high due to the association through hydrogen bonds: two molecules of the carboxylic acid are held together by two hydrogen bonds rather than one.



- Aromatic carboxylic acids burn with a yellow smoky flame whereas aliphatic ones burn with a blue flame without smoke.

Chemical properties

The acidic properties of carboxylic acids are attributed to the proton of the carboxyl group. Mono carboxylic acids are weak acids except formic acid, which is the strongest. The tendency of the alkyl group to release electrons weakens the acid; thus formic acid is the strongest. On the other hand presence of electron withdrawing groups (such as halogens) especially on the alpha carbon increases the acidity.

Reactions of carboxylic acids are related to:

- the proton as in salt formation reactions.
- removal of the hydroxyl group as in conversion to derivatives such as esters, amides, or acid chlorides.
- substitution either in the alpha position of aliphatic acids or in the meta position of aromatic ones.

> ❖ **Give an example of a carboxylic acid with *α*-halogenation (name and chemical structure). Which parameter will you look for to compare its acidity with other acids?**
> ❖ **Give the general formula of esters, amides, and acid chlorides.**

Chemical reactions

1. General test (Ferric chloride test)

The acid solution should be made neutral before performing the test with ferric chloride solution. This is achieved by adding very dilute ammonia solution drop by drop with shaking to a solution of about 0.5 g of the solid acid or 2 drops of the liquid acid in 1 mL water until the medium becomes basic as indicated by changing the colour of litmus paper to blue or changing the colour of phenolphthalein indicator from colorless to pink, in which case the characteristic odour of ammonia is predominant. At this stage the solution is slightly basic. To make the

solution neutral the excess ammonia should be removed by gently heating the test tube in a water bath with shaking from time to time until both the odour of ammonia and the pink colour disappears. (In case of oxalic, tartaric, citric and lactic acids keep a portion of their neutral solution for use in calcium chloride test). Cool the solution and then add few drops of ferric chloride solution to get different colours (solutions or precipitates) as follows:

acid	result
formic and acetic	**red solution**
succinic and benzoic	**light brown precipitate**
salicylic	**violet solution**
oxalic, tartaric, citric, and lactic	**no special change**

The steps of this test are:

$$NH_4OH + RCOOH \longrightarrow \underset{\substack{\text{ammonium salt}\\ \text{of the acid}\\ \text{(neutral solution)}}}{RCOONH_4} + H_2O$$

$$\underset{\text{neutral solution}}{3RCOONH_4} + FeCl_3 \longrightarrow \underset{\substack{\text{ferric salt of}\\ \text{the acid}}}{(RCOO)_3Fe} + 3NH_4Cl$$

When the solution is ***basic*** (excess ammonia):

$$FeCl_3 + \underset{\text{excess ammonia}}{3NH_4OH} \longrightarrow \underset{\substack{\text{ferric hydroxide}\\ \text{(brown orange ppt.)}}}{Fe(OH)_3} + 3NH_4Cl$$

$$FeCl_3 + 3RCOOH \xrightarrow[\text{excess}]{NH_4OH} (RCOO)_3Fe + Fe(OH)_3$$

Therefore elimination of the excess ammonia is important since the brown orange precipitate of ferric hydroxide formed by this excess interferes with the colour of the ferric salt of the acid resulting in a false result.

If the solution is still ***acidic*** (little ammonia is added), colourless complexes are formed between the acid and ferric ions, a false negative result.

$$FeCl_3 + 3RCOOH \xrightarrow{\text{acidic medium}} (RCOOH)_3Fe$$

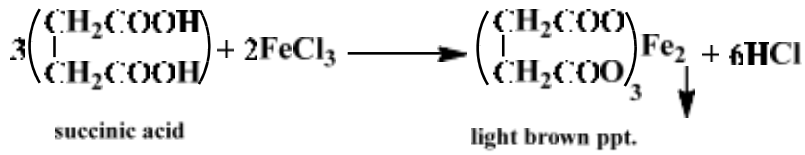
colourless soluble complex

As mentioned in the above table formic acid and acetic acid form a red coloured solution in this test:

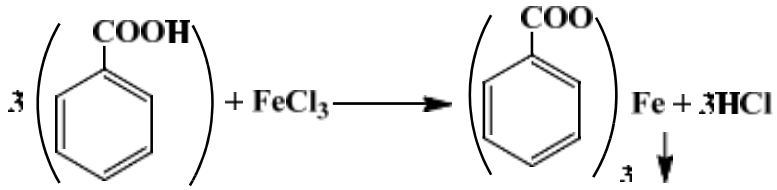
$$3HCOOH + FeCl_3 \longrightarrow (HCOO)_3Fe + 3HCl$$

formic acid — red colour

Succinic acid and benzoic acid give a light brown precipitate:



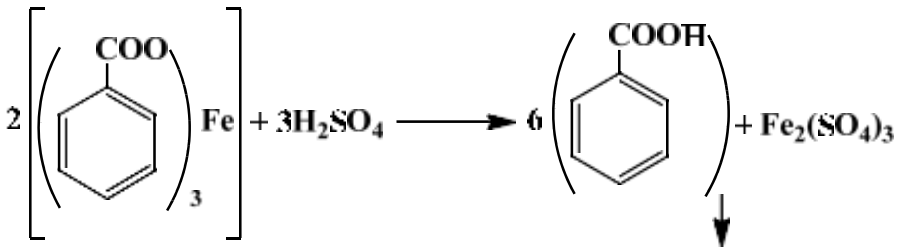
succinic acid — light brown ppt.



benzoic acid — light brown ppt.

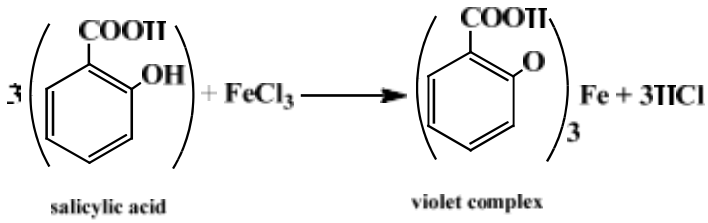
To distinguish between these two acids add few drops of dilute sulphuric acid to this light brown precipitate with shaking thereby liberating the free carboxylic acid back. If the liberated acid is water soluble then it is succinic acid which is aliphatic. On the other hand benzoic acid is liberated as a white precipitate because it is insoluble in water since it is aromatic.

light brown ppt. — dilute — soluble succinic acid



light brown ppt. — dilute — insoluble white ppt. (benzoic acid)

Salicylic acid gives a violet colour:

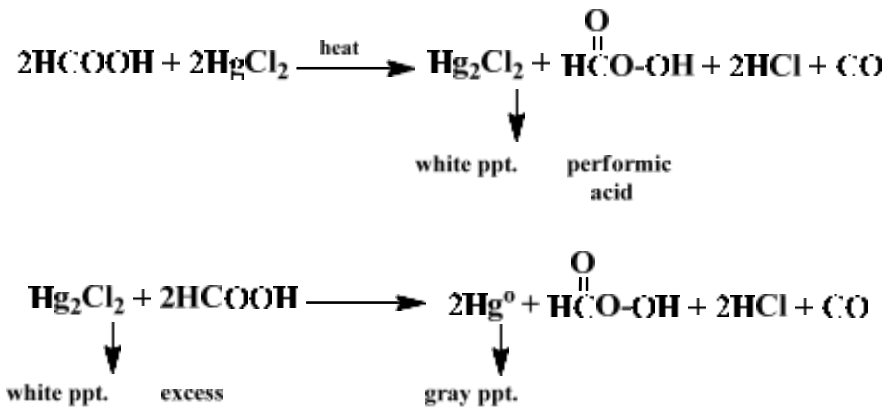


2. Special tests for formic acid

Since formic acid has a hydrogen attached to the carbonyl group (HC=O) it can reduce certain compounds while being oxidized:

a) Reduction of mercuric chloride

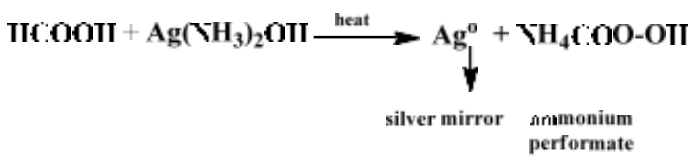
Formic acid reduces mercuric chloride to mercurous chloride in the form of white precipitate and, in the presence of excess acid, mercurous chloride is reduced to mercury element as a gray precipitate.



To few drops of the acid add few drops of mercuric chloride solution, and then heat to get a white precipitate. Add excess of the acid with heating to get the gray precipitate of elemental mercury.

b) Tollen's test

Refer to the experiment of identification of aldehydes and ketones for preparation of Tollen's reagent and procedure of this test.



c) Alkaline potassium permanganate test

Formic acid reacts with potassium permanganate solution, a strong oxidizing agent, in alkaline medium causing decolourization of this violet reagent.

Mix 2–3 drops of the acid with 5 mL of sodium bicarbonate solution, and then add 1% potassium permanganate solution drop by

drop and observe the disappearance of the original violet colour of the reagent which will be followed by the appearance of a brown precipitate of manganese dioxide.

$$HCOOH + KMnO_4 \xrightarrow{NaHCO_3} MnO_2 + H_2O + CO_2$$

brown ppt.

3. Special test for acetic acid (ester formation)

Acetic acid, on contrary to formic acid, neither can be oxidized by, nor can reduce any of the reagents applied to formic acid. Instead, it undergoes ester formation reaction:

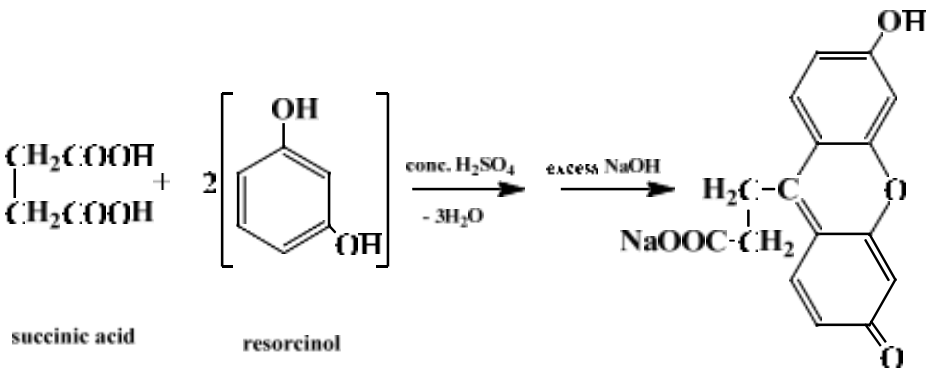
$$CH_3COOH + C_2H_5OH \underset{}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

ethyl acetate
(ester)

Mix 1 mL of acetic acid with 2 mL of ethanol in a test tube and add to this mixture 2–3 drops of concentrated sulphuric acid. Heat the test tube in a water bath for 10 minutes, and then pour the mixture into another test tube containing 5 mL sodium bicarbonate solution; the characteristic fruity odour of ethyl acetate can be smelt, which indicates the formation of this ester.

4. Special test for succinic acid (Fluorescence test)

In a dry test tube mix equal quantities of succinic acid and resorcinol with 2 drops of concentrated sulphuric acid. Heat the mixture on direct flame for 1 minute until the mixture melts. Cool and add excess of 10% sodium hydroxide solution to get a red colour with green fluorescence. If the colour is not so clear dilute with water.



succinic acid

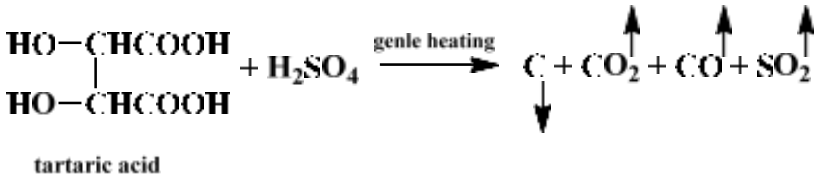
resorcinol

red colour with
green fluorescence

5. Special tests for tartaric acid

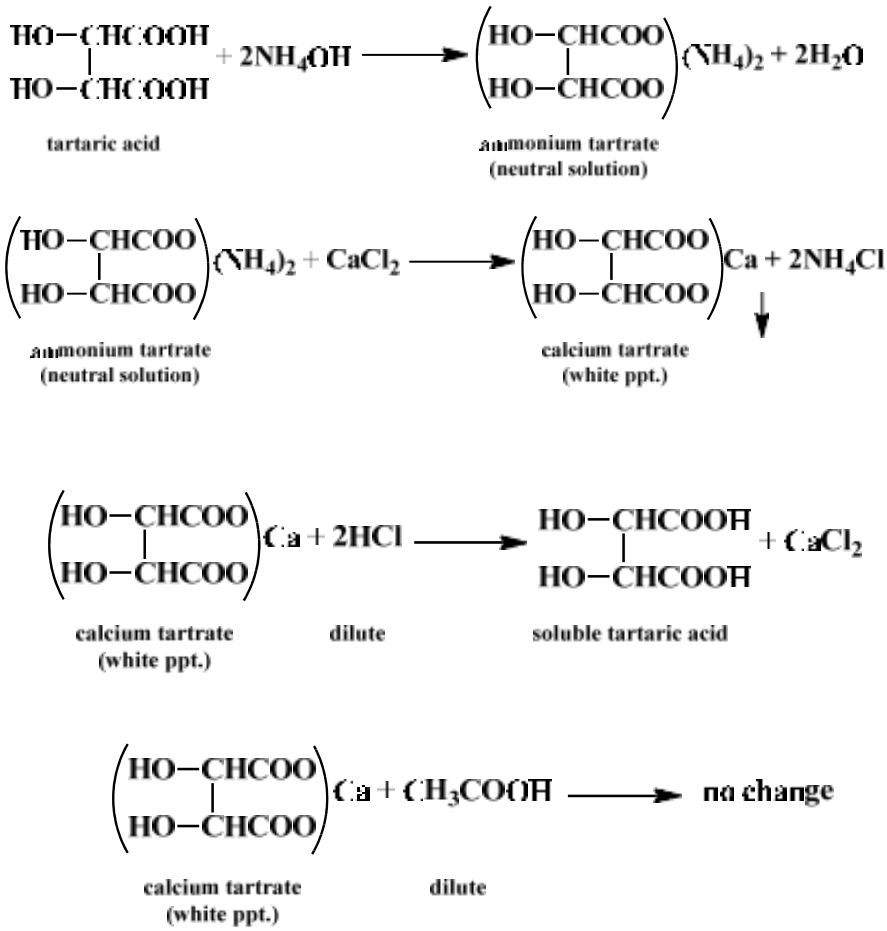
a) Reaction with concentrated sulphuric acid

When a mixture of about 0.5 g of tartaric acid and 1 mL of concentrated sulphuric acid is heated gently on a flame with shaking heavy charring takes place and carbon monoxide, carbon dioxide, sulphur dioxide gases are evolved.



b) Reaction with calcium chloride solution

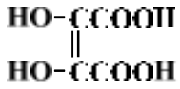
To about 1 mL of the cold neutral solution of the tartaric acid (see the general test) add few drops of calcium chloride solution; a white precipitate of calcium tartrate is formed. This precipitate dissolves in dilute hydrochloric acid but not in dilute acetic acid.



c) Reaction with Fenton's reagent

Dissolve about 0.5 g of tartaric acid in 1 mL of water and then add 1 drop of ferrous sulphate solution followed by 2 drops of hydrogen peroxide solution. Then add excess of 10% sodium hydroxide solution until an intense violet colour is observed.

In this reaction the components of Fenton's reagent (hydrogen peroxide and iron) undergo an oxidation-reduction reaction that results in the generation of ferric ions which form ferric salt of dihydroxyfumaric acid that is responsible for the violet colour.



dihydroxyfumaric acid

6. Special tests for oxalic acid

a) Reaction with potassium permanganate solution

Oxalic acid reacts with acidic potassium permanganate solution causing decolourization of this reagent. It doesn't react with this reagent under alkaline medium.

Dissolve 0.5 gm of the acid in 2–3 mL of distilled water and add 2–3 mL of dilute sulfuric acid. Heat gently (water bath), and then add potassium permanganate solution drop by drop and observe the disappearance of the violet color of the reagent.

$$5\begin{pmatrix} COOH \\ | \\ COOH \end{pmatrix} + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

oxalic acid dilute

b) Reaction with calcium chloride solution

For procedure follow the same steps mentioned above for tartaric acid. The same results are obtained.

c) Reaction with concentrated sulphuric acid

For procedure follow the same steps mentioned above for tartaric acid. The same gases are bubbled out with a little darkening.

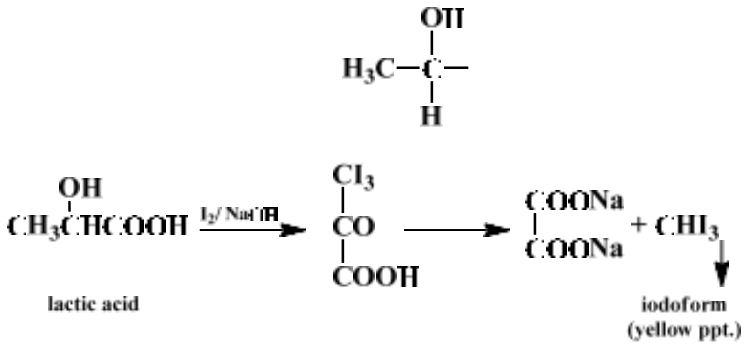
d) Reaction with Fenton's reagent

For procedure follow the same steps mentioned above for tartaric acid. Oxalic acid gives negative result with this reagent.

7. Special tests for lactic acid

a) Iodoform test

Lactic acid can undergo iodoform formation reaction since it contains a free methyl group and a hydrogen attached to the carbon bearing the hydroxyl group:



For procedure follow the same steps mentioned in the identification of alcohols experiment.

b) Reaction with concentrated sulphuric acid

For procedure follow the same steps mentioned above for tartaric acid. The same gases are bubbled out with a considerable blackening but without a marked charring.

c) Reaction with calcium chloride solution

For procedure follow the same steps mentioned above for tartaric acid. Lactic acid gives negative result.

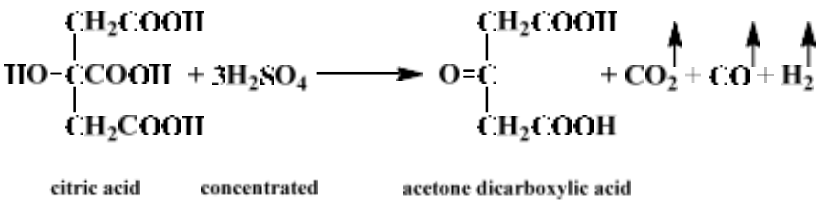
d) Reaction with Fenton's reagent

For procedure follow the same steps mentioned above for tartaric acid. Lactic acid gives negative result with this reagent.

8. Special tests for citric acid

a) Reaction with concentrated sulphuric acid

For procedure follow the same steps mentioned above for tartaric acid. The same gases are bubbled out and the mixture turns to yellow but does not char. Acetone dicarboxylic acid is also formed, and its presence is tested by heating the mixture for 1 minute, cool, add a few milliliters of water and make alkaline with 30% sodium hydroxide solution. Add a few milliliters of sodium nitroprusside solution and observe the intense red colouration of the medium.



b) Reaction with calcium chloride solution

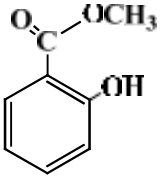
For procedure follow the same steps mentioned above for tartaric acid. Citric acid gives the same results.

c) Reaction with Fenton's reagent

For procedure follow the same steps mentioned above for tartaric acid. Citric acid gives negative result with this reagent.

9. Special test for salicylic acid (ester formation)

In addition to the characteristic violet colour obtained with ferric chloride, salicylic acid can also be detected by ester formation test. In this test methyl salicylate ester separates out as an organic phase having a characteristic odour.



methyl salicylate

Follow the same procedure and conditions used for esterification of acetic acid but use methanol instead of ethanol. Not that *methanol is toxic internally* so never withdraw it by mouth to avoid accidental ingestion.

- **Methyl salicylate, also known as *wintergreen oil*, is used widely in pharmaceutical topical preparations, give its main use with the name of a popular topical preparation.**
- **Both ethyl acetate and methyl salicylate separate as an organic phase during ester formation test, how can you detect the organic layer practically and theoretically?**
- **Fill the following table:**

acid	tests results with description			
	$FeCl_3$ test	H_2SO_4 test	$CaCl_2$ test	Fenton's test
citric				
oxalic				
tartaric				
lactic				