1. CARBOXYLIC ACIDS

Introduction

Carboxylic acids are organic compounds that have a carboxyl group attached to an alkyl group (**R**COOH) or to an aryl group (**Ar**COOH). 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. **See figure 1.**

Physical Properties

Formic acid, acetic acid, and lactic acid are liquids at room temperature; while succinic acid, citric acid, salicylic acid, phthalic acid and tartaric acid are solids at room temperature. **See figure 1**.
Low molecular weight carboxylic acids are soluble in water and, therefore, lie under class **S1**. Water insoluble acids dissolve in both sodium hydroxide solution and sodium bicarbonate solution, being classified under class **A1**. When they react with sodium bicarbonate, they evolve carbon dioxide gas. ***This is considered as a good simple indication of them.*** **See EFFERVESCENT TEST**.
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. **See figure 2**.
Aromatic carboxylic acids burn with a yellow smoky flame whereas aliphatic ones burn with a blue flame without smoke. ***In figure 1: determine aliphatic and aromatic carboxylic acids.***

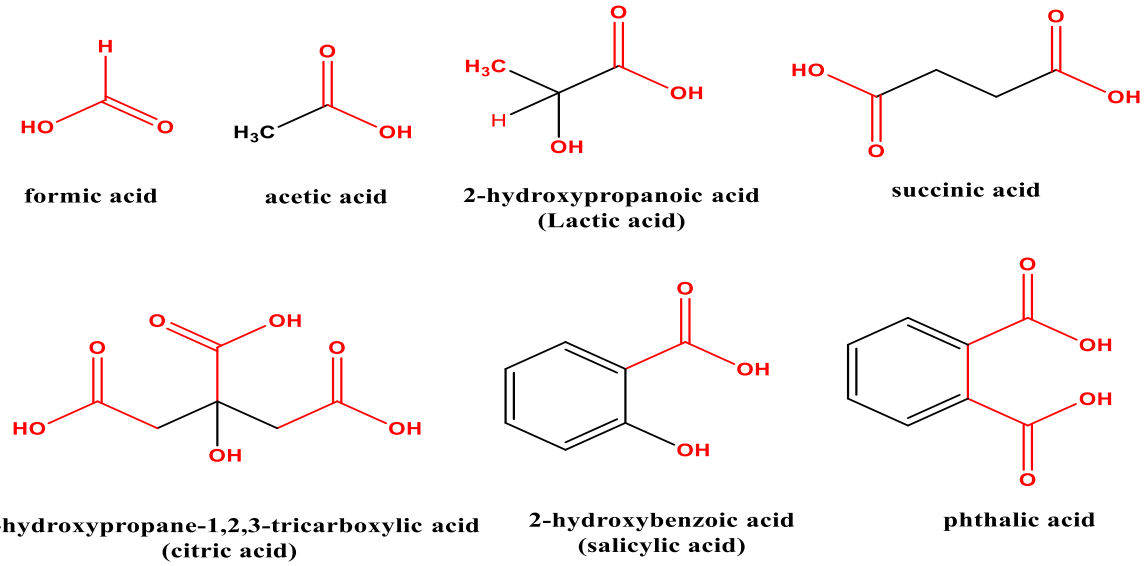


Figure 1: some examples of carboxylic acids.

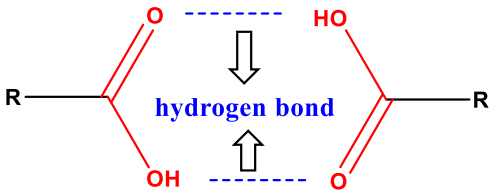


Figure 2: hydrogen bonds between two molecules of carboxylic acid.

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, e. g. trifluoroacetic acid.* **See figure 3.**

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.*

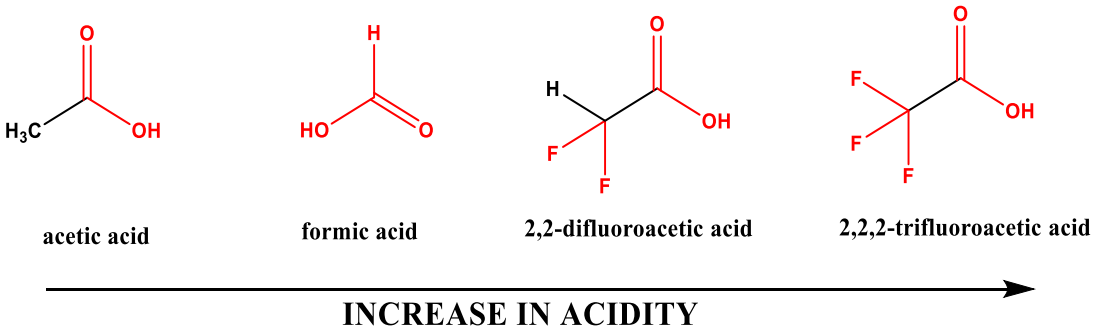


Figure 3: arrangement of some carboxylic acid according to their acidity.

Identification Of Carboxylic Acids

1st: GENERAL TESTS

any carboxylic acid will give positive result with the following tests

1. pH of AQUEOUS SOLUTION

PROCEDURE

Compounds that are soluble in water

simply prepare an aqueous solution and check the pH with pH paper. If the compound is an acid, the solution will have a low pH.

Compounds that are insoluble in water

can be dissolved in ethanol (or methanol) and water. First, dissolve the compound in the alcohol, and then add water until the solution just becomes cloudy. Clarify the solution by adding a few drops of the alcohol, and then determine its pH using pH paper.

NOTE: *phenols are also acidic compounds and give positive results with this test*.

2. SODIUM BICARBONATE TEST (EFFERVESCENT TEST)

PROCEDURE

Dissolve a small amount of the compound in a **5 or 10% aqueous sodium bicarbonate** solution. Observe the solution carefully. If the compound is an acid, you may see bubbles of carbon dioxide form. In some cases with solids, the evolution of carbon dioxide may not be that obvious but the compound will be dissolved.

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2CO_3 \text{ (unstable)}$$
$$H_2CO_3 \longrightarrow CO_2\uparrow + H_2O$$

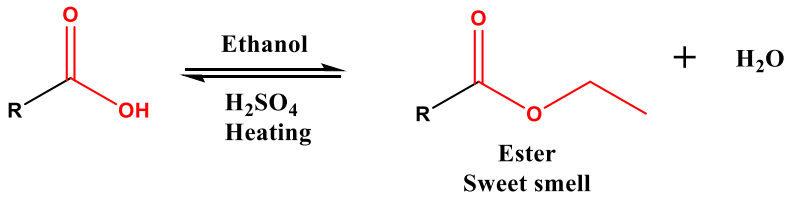
***NOTE**: phenols will not give positive results with this test only in few exceptions. Phenols can be eliminated either by the ferric chloride test or by spectroscopy (phenols have no carbonyl group).*

3. ESTERIFICATION TEST

This test based on the fact that carboxylic acids react with alcohol (in our procedures will use absolute ethanol) in the presence of concentrated H_2SO_4 producing sweet smelling esters (positive results); this test can be used to make specific identification of acetic acid and salicylic acid.

PROCEDURE

Mix **1mL** or **0.1g** of acid with **2mL** of ethanol in a test tube and add to this mixture **2-3 drops** of concentrated sulfuric acid. Heat the test tube in a water bath for **5 minutes**, and then pour the mixture into another test tube containing **5mL of 10% sodium bicarbonate** solution; the formation of sweet smelling indicates the formation of ester.



Identification Of Carboxylic Acids

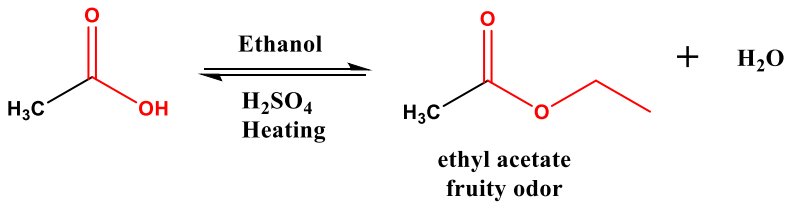
2nd: SPECIAL TESTS

In this section we will try to identify specific carboxylic acid because general test will only give general idea about the compound.

1. ACETIC ACID → ESTERIFICATION TEST

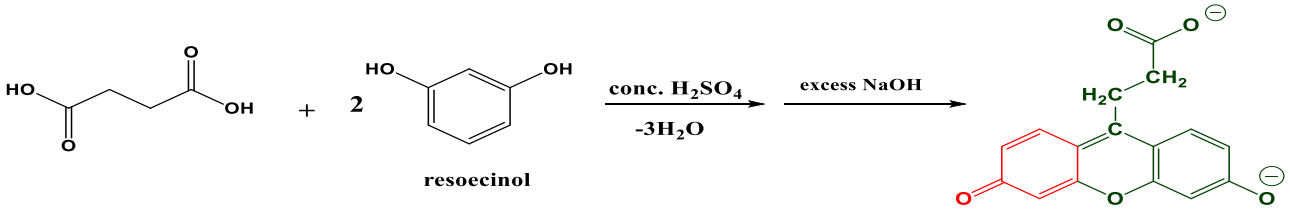
PROCEDURE

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

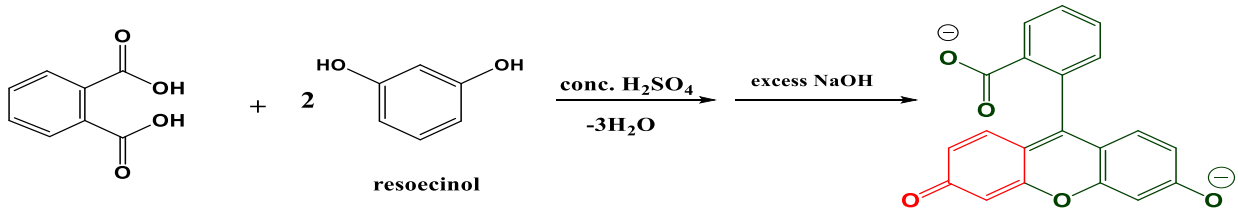


2. 1,2-DICARBOXYLIC ACIDS → FLUORESCENCE TEST

Succinic acid and phthalic acid will give positive results (Fluorescence test).



red color with green fluorescence



fluorescein

PROCEDURE

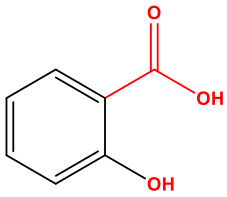
In a dry test tube mix **0.1g** of succinic acid or phthalic acid and **0.2g** of resorcinol and add **2drops** of concentrated sulfuric acid. Heat the mixture on oil bath for **1-2 minutes** until the mixture melts. Cool and add excess of **10% sodium hydroxide** solution to get a ***red color with green fluorescence***. If the colour is not so clear dilute with water.

NOTE: *only 1,2-dicarboxylic acid will give this test other types will not give positive results.*

3. SALICYLIC ACID

a. FERRIC CHLORIDE TEST

Because salicylic acid has phenolic group so it will give positive result (violet color) with neutral ferric chloride test.



PROCEDURE

Place the small amount of the unknown compound in dry test tube and dissolve it by adding small quantity of methanol; then add **2 drops** of neutral ferric chloride solution

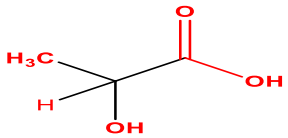
and observe the formation of violet color which indicate the presence of phenolic group in the unknown compound.

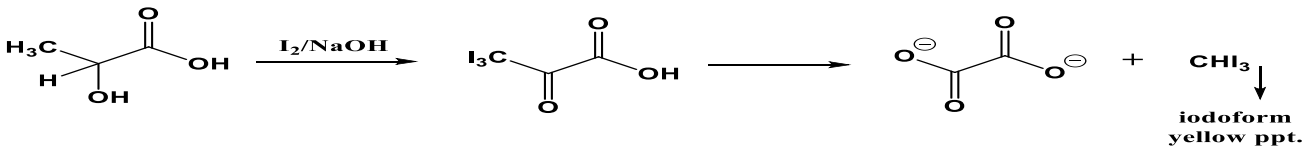
b. ESTERIFICATION TEST

see procedure mentioned with acetic acid but use methanol instead of ethanol. ***You will smell characteristic odor of methyl salicylate which separate out as organic phase.***

4. LACTIC ACID → 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****.*





PROCEDURE

a. Dissolve the compound (**2-3 drops or 100mg**) in water (**2-3ml**) in a test tube and add **1ml of 10% sodium hydroxide**.

b. To this add a saturated solution of iodine-potassium iodide in water with stirring until the dark colour of iodine persists.

c. Heat the solution in a **boiling water bath** for **1-2 minutes** or **hot water bath for 5 minutes**; shaking the test tube occasionally. It is likely that some or all of the dark color of the iodine reagent will be discharged.

d. If the dark color of the iodine reagent is still apparent following heating, add **dropwise 10% sodium hydroxide** solution until the dark color of the iodine reagent has been discharged. Shake the mixture in the test tube (corked) during the addition of sodium hydroxide. Care need not be taken to avoid adding excess sodium hydroxide.

e. After the dark iodine color of the solution has been discharged, fill the test tube with water to within **2cm** of the top. Cork the test tube and shake it vigorously.

Allow the tube to stand for at least **15 minutes** at room temperature. The appearance of a pale yellow precipitate of iodoform constitutes a positive test.

f. The yellow precipitate usually settles out slowly onto the bottom of the test tube. Sometimes, the yellow color of iodoform is masked by a dark substance.

NOTEs

1. Use dioxane to dissolve the compound if it is water insoluble.
2. If the iodoform is dark reddish yellow in colour, dissolve it in **3-4ml** of dioxane and treat it with **1ml of 10% sodium hydroxide** solution, shake until a light yellow solid remains. Dilute with water and filter the solid.

Home Work
Give an example of a carboxylic acid with a 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.