

14.1 ALIPHATIC AND AROMATIC CARBOXYLIC ACIDS

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Learning outcomes

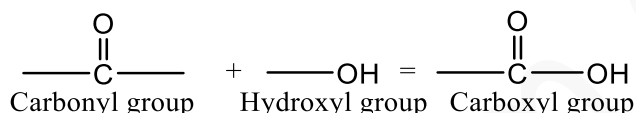
After the lesson, learners should be able to:

- Describe briefly the nomenclature and isomerism of aliphatic and aromatic carboxylic acids.
- Show the preparation of monocarboxylic acids from: aldehydes, nitriles, dicarboxylic acids, sodium alkoxide, and trihaloalkanes.
- Show the preparation of benzoic acid from alkylbenzene.
- State physical properties of monocarboxylic acids.
- Explain the chemical properties of aliphatic and aromatic carboxylic acids: Action with alkalis, metal oxides, metal carbonates, metal bicarbonates, PCl_3 , LiAlH_4 , and dehydration of carboxylic acids; Hell-Volhard-Zelinsky reaction.
- Electrophilic substitution reaction of benzoic acid (bromination, nitration, and sulphonation).
- Explain the effect of constituents on the acid strength of carboxylic acid.
- Describe the abnormal behaviour of methanoic acid.

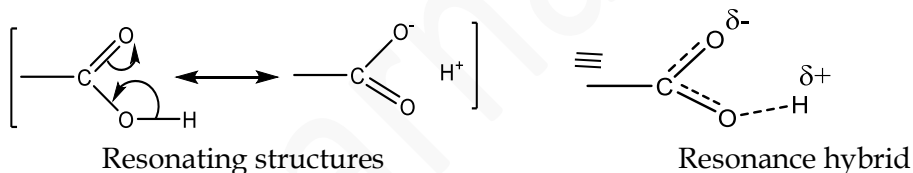
Introduction

The organic functional group **-COOH** is called the carboxyl group because it is formed by the combination of the carbonyl group ($>\text{CO}$) and hydroxyl group ($-\text{OH}$).

Its structure is

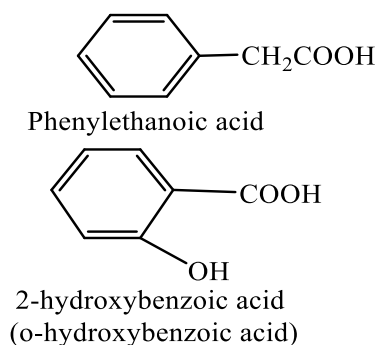
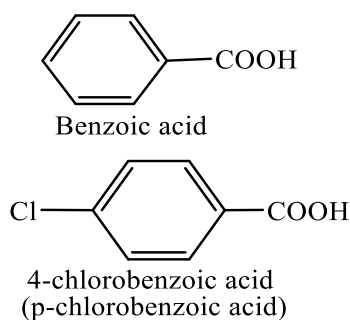


However, due to resonating structures, compounds containing the carboxyl group have entirely different properties than both carbonyl compounds and alcohols.



Carboxylic acid is one of the reactive functional groups among the organic compounds.

Carboxylic acids are named by adding the **-oic acid** as a secondary suffix, replacing -e in the name of the parent hydrocarbon alkane, i.e., alkanoic acid.



Isomerism

I. Functional Isomerism

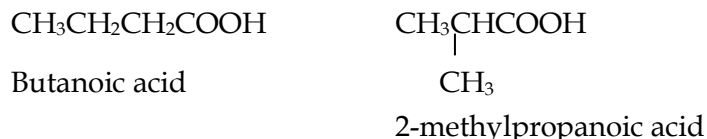
Carboxylic acids can form functional isomers with esters.

e.g. $C_2H_4O_2$ can exist as;



II. Chain Isomerism

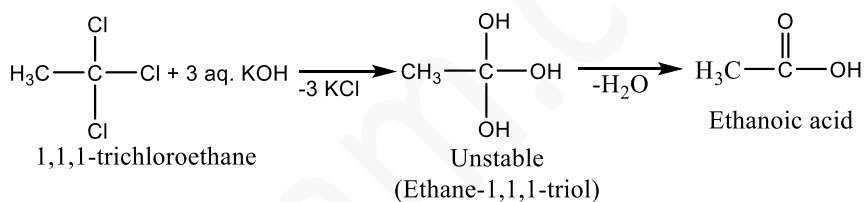
Chain isomerism is possible in carboxylic acids containing four or more carbon atoms. e.g., the following two isomers are possible for the formula $C_4H_8O_2$.



General methods of preparation of monocarboxylic acids

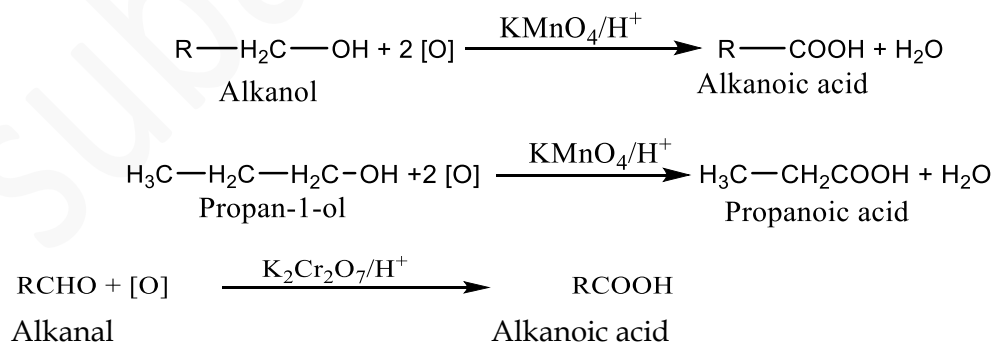
I. From trihaloalkanes

Hydrolysis of 1,1,1-trihaloalkanes produces unstable trihydroxy alkanes which undergo dehydration to give monocarboxylic acid.



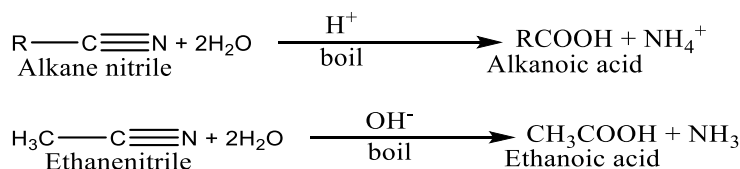
II. By oxidation of 1° alcohols and aldehydes (studied in alcohols and aldehydes- ketones chapters already)

Primary alcohols and aldehydes oxidise in the presence of strong oxidising agents such as alkaline or acidified $KMnO_4$, $K_2Cr_2O_7$, etc., to give carboxylic acids.



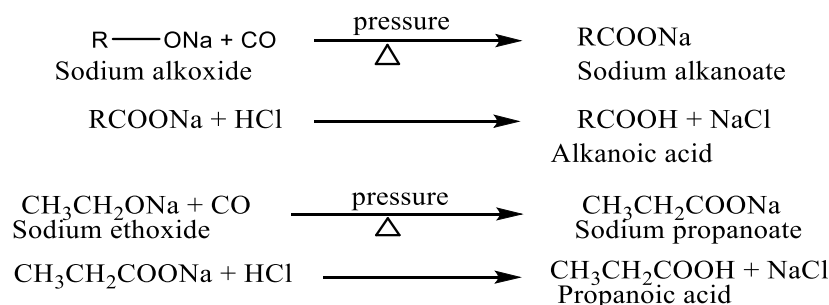
III. By hydrolysis of nitriles

Alkanenitriles, on acidic or basic hydrolysis, produce acids (via amide and ammonium salt).



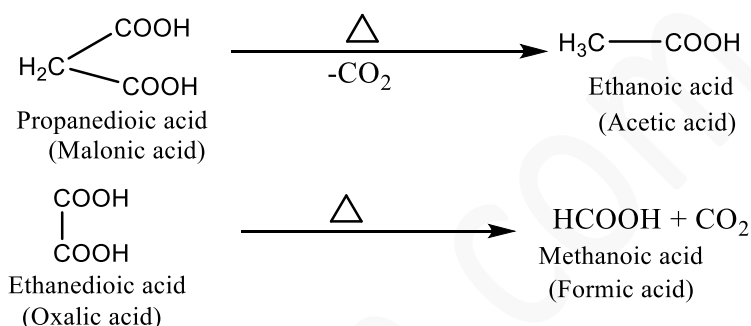
IV. From sodium alkoxide

Sodium alkoxide, when heated with carbon monoxide under pressure, gives sodium alkanoate, which on acidification gives carboxylic acids.



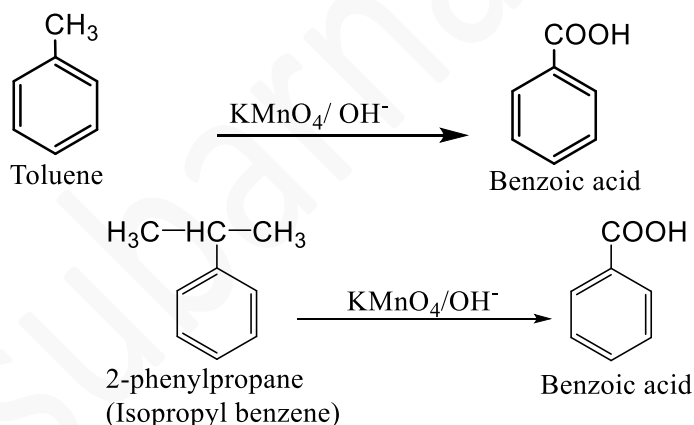
v. From dicarboxylic acids

Dicarboxylic acids, when heated, yield monocarboxylic acids and carbon dioxide gas. This reaction is also known as **decarboxylation**.



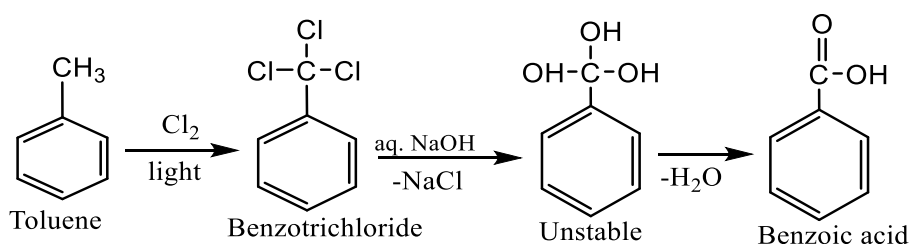
Preparation of Benzoic acid from alkyl benzene

Irrespective of the chain length of the alkyl group, alkyl benzenes are oxidised by **alkaline KMnO₄** or **dil. HNO₃** as an oxidising agent into benzoic acid.



Manufacture of Benzoic acid

Benzoic acid is prepared on an industrial scale by bubbling chlorine through the boiling toluene in the presence of ultraviolet light. The benzotrichloride obtained is hydrolysed by alkali to benzoic acid.

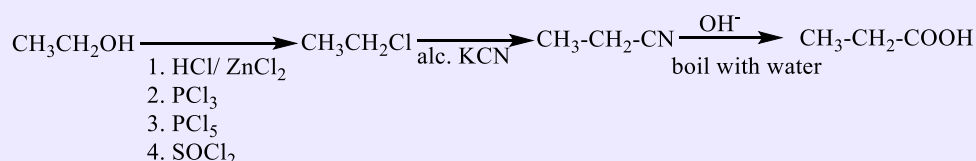


Worked Example

1. Convert Ethanol to Propanoic acid.

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Solution:



Physical properties

I. State:

The first few members are liquids and higher members are waxy solids because the intermolecular force of attraction increase with increasing molecular mass.

II. Solubility

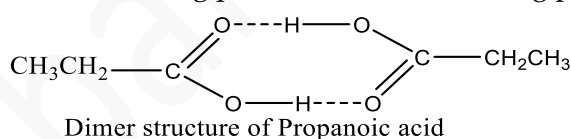
The lower members of carboxylic acids are highly soluble in water owing to their polar nature and the capacity to form hydrogen bonds with water.

But the solubility decreases gradually moving up the homologous series as the non-polar alkyl part gets bigger and hence dominant.

III. Melting and boiling points

The melting and boiling points of carboxylic acids are higher relative to corresponding compounds of other classes of organic compounds of comparable molecular mass. This is because of strong hydrogen bonds formed between two molecules, which result in dimers, making the effective molecular mass double. e.g.

CH_3COOH	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
Molecular wt = 60	Molecular wt = 60	Molecular wt = 58
Boiling point = 118°C	Boiling point = 97°C	Boiling point = -1°C

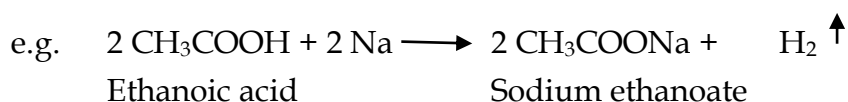
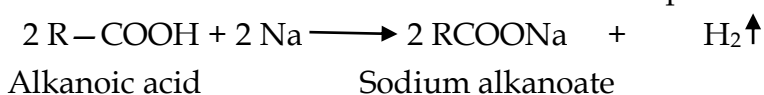


Chemical properties

1. Acidic nature

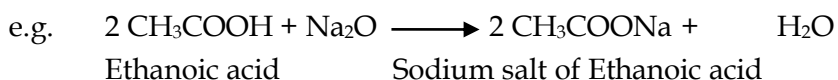
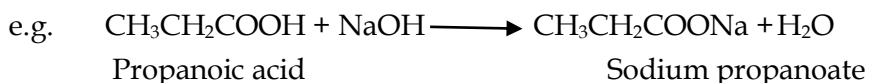
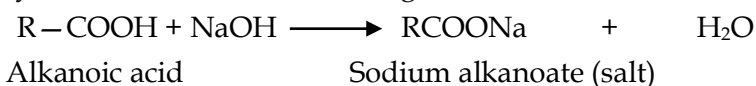
2. Reaction with active metal (Na)

Active metals like alkali and alkaline earth metals replace hydrogen from acids.



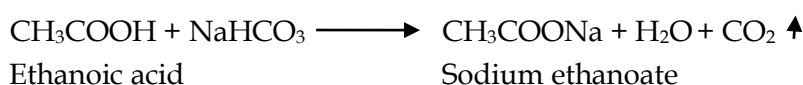
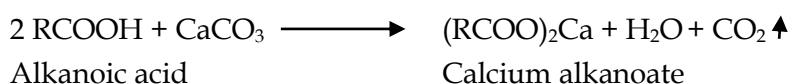
3. Reaction with base (NaOH or Na₂O etc.)

Carboxylic acids react with a base to give salt and water.



4. Reaction with metal carbonates and bicarbonates

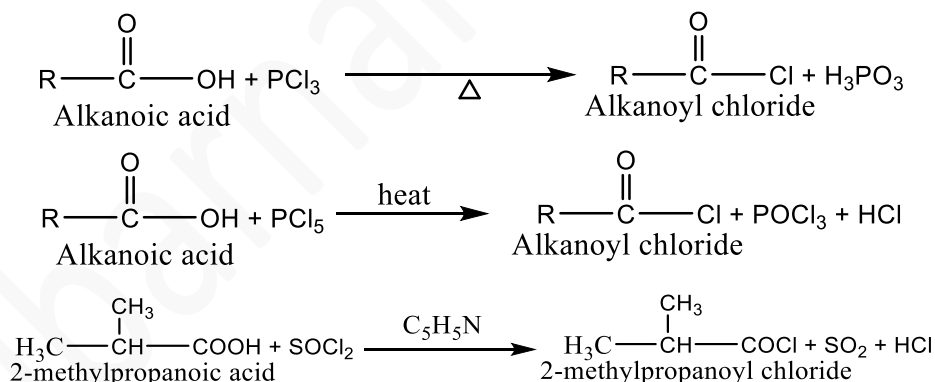
Carboxylic acids react with metal carbonates and bicarbonates, evolving carbon dioxide gas. This reaction is used for the test of the carboxylic acid functional group in organic compounds.



2. Reaction involving -OH group

1. Reaction with PCl₃

The hydroxyl group of the carboxylic acid is replaced by the chloride group, forming acid chloride on treatment with these reagents in the presence of pyridine.

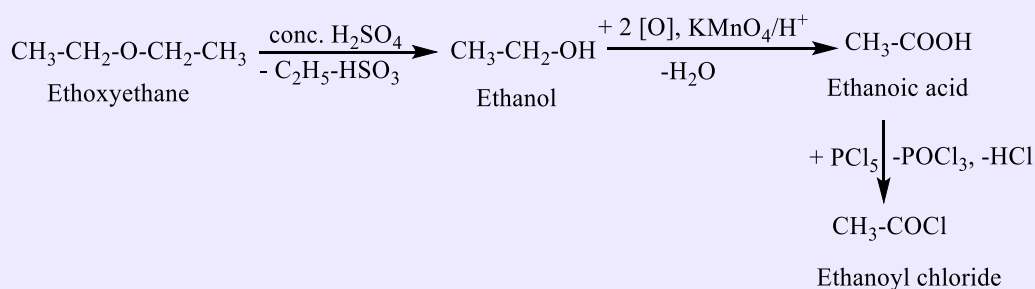


Worked Example

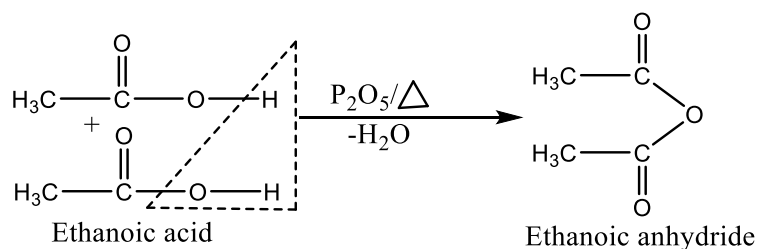
2. Convert Ethoxyethane to Ethanoyl chloride.

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Solution:



2. Dehydration (Formation of acid anhydrides - reaction with P₂O₅)



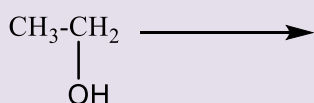
3. Consider the following reaction

The compound A is a primary alcohol which gives the iodoform test. Identify the organic compounds A, B, C, D and E, giving the complete reaction sequence.

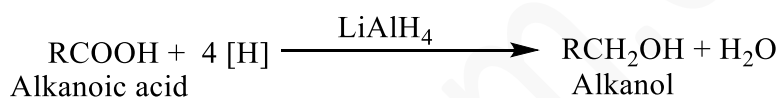
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{Hint:

The only primary alcohol that gives the iodoform test is Ethanol. Therefore, A must be Ethanol.



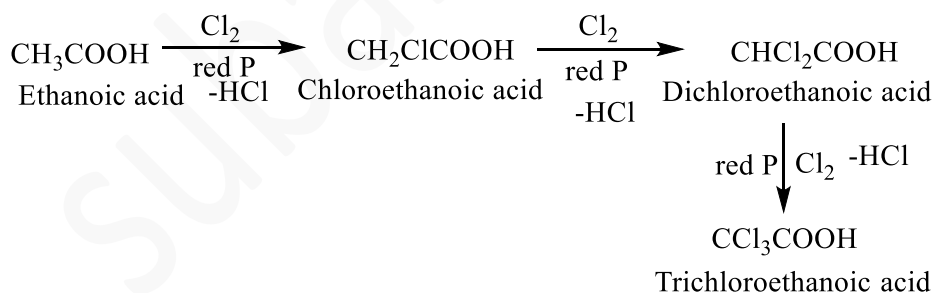
5. Reduction with LiAlH₄ (partial reduction)



3. Reaction involving side chain (alkyl group)

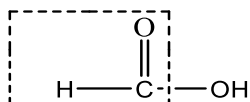
1. Halogenation of side chain (Hell-Volhard-Zelinsky -HVZ reaction)

When carboxylic acids are treated with Cl₂ or Br₂ in the presence of red phosphorus, all the α-hydrogen atoms of carboxylic acids are replaced successively by the halogen atoms.



Abnormal properties of Formic acid

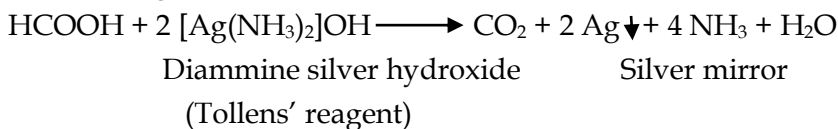
Formic acid or Methanoic acid, apart from being a carboxylic acid, resembles somewhat an aldehyde functional group. Thus, it gives a few reactions which other carboxylic acids don't.



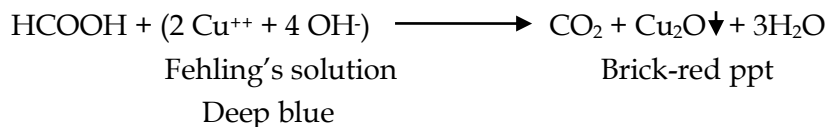
Therefore, formic acid can be distinguished from other acids by the following chemical reactions.

I. Reaction with Tollens' reagent

Formic acid gives a silver mirror with ammoniacal silver nitrate (Tollens' reagent).



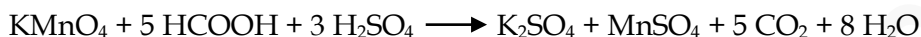
II. Reaction with Fehling's solution



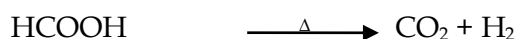
III. Reaction with conc. H_2SO_4



IV. Reaction with acidified KMnO_4



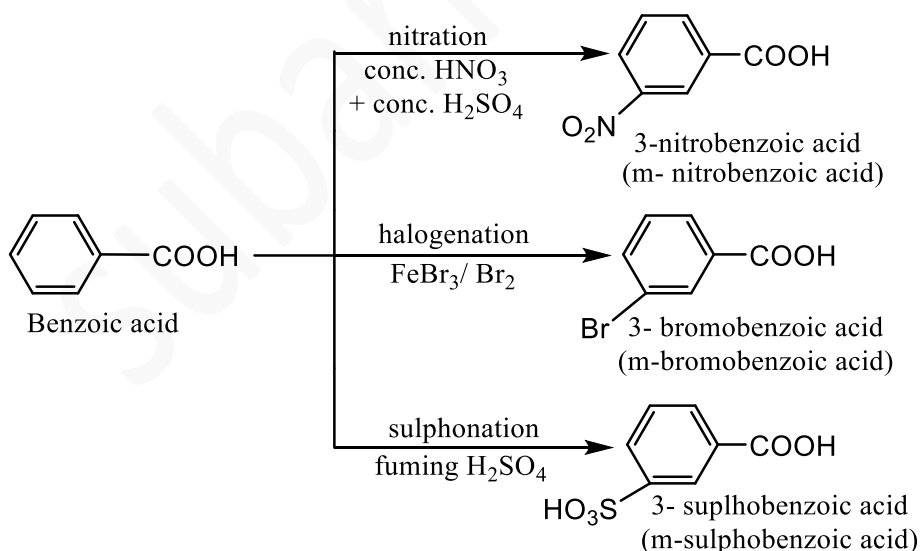
V. Action of heat



Electrophilic aromatic substitution reaction of Benzoic acid

The carboxylic group is an electron-withdrawing group and meta director; therefore undergo nitration, sulphonation and halogenation reactions at the meta position with difficulty.

 **Remember:** $-\text{COOH}$ is an electron-withdrawing group and a meta director.



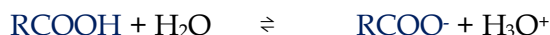
Acidity of Carboxylic acids

The acidity of carboxylic acids can be explained based on the following two facts:

Ionisation constant

In water, carboxylic acids ionise partially to form hydronium ions and carboxylate ions. A stronger acid has a greater tendency to ionise.

The dissociation of a carboxylic acid can be represented as:



The equilibrium (K_c) of the process is given by the expression:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}]}$$

A stronger acid has a larger K_a . The value of K_a , therefore, the acidity decreases in the following order.

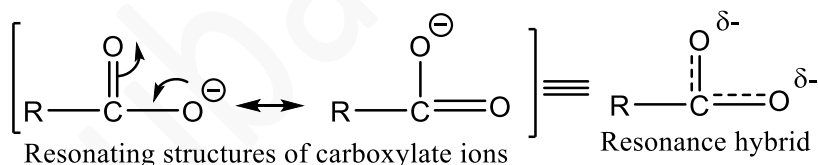
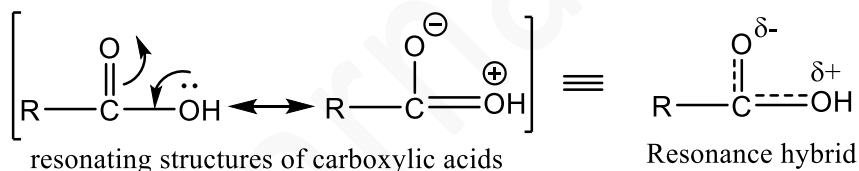
Formic acid > Acetic acid > Propionic acid > n-butyric acid

Trichloroacetic acid > Dichloroacetic acid > Chloroacetic acid > Acetic acid

Resonance stabilisation

Carboxylic acids are quite strong acids because of the presence of a polar O-H group. They ionise to give protons.

Carboxylic acids as well as their carboxylate anion are both stabilised by resonance.



However, the carboxylate anion is more stabilised by resonance because its contributing structures are exactly identical and do not include charge separation as in carboxylic acid. Therefore, the above equilibrium lies very much towards the ionised form.

Carboxylic acids are weak acids because they ionise only partially in water. However, they are stronger acids than alcohols and phenols because the carboxylate ion is stabilised by resonance.

Effects of Substitution on Acidity of Carboxylic Acids

The factors which increase the stability of the carboxylate ion more than the carboxylic acid increase the acid strength.

Therefore, electron-withdrawing groups stabilise the carboxylate ion by dispersal of the negative charge and increase the acid strength. On the other hand, electron-releasing groups destabilise the carboxylate ion and decrease the acid strength.

Remember

Increasing electron-releasing alkyl groups → decreasing acidity

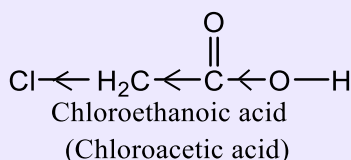
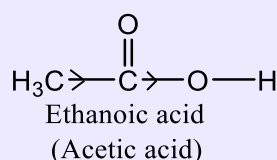
Increasing electron-withdrawing Cl atoms → increasing acidity

Worked Example

4. Why is chloroacetic acid a stronger acid than acetic acid? 2

Solution:

The greater the tendency of an acid to release a proton, i.e., H^+ ion, the stronger the acidic character. In acetic acid, the methyl group is an electron-releasing group; due to this, the proton of the acid does not lose easily, but in chloroacetic acid, chlorine is an electron-withdrawing group and withdraws electrons; due to this, the proton of the acid is lost easily. Therefore, chloroacetic acid is a stronger acid than acetic acid.

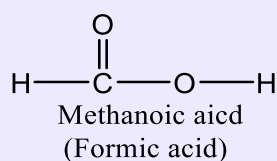
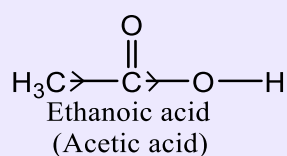


Worked Example

5. Why is ethanoic acid weaker than Methanoic acid? 2

Solution:

The greater the tendency of an acid to release a proton, i.e., H^+ ion, the stronger the acidic character. The electron-releasing methyl group destabilises the carboxylate ion, making ionisation less favorable. Therefore, ethanoic acid is weaker than methanoic acid. Therefore, acetic acid is a weaker acid than formic acid.



In other words, the carboxylate ion of acetic acid is destabilised by the electron-releasing methyl group in comparison to formic acid. That makes acetic acid a weaker acid than formic acid.

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