

Carboxylic Acids

The compounds containing the carboxyl functional group -COOH are called Carboxylic acids. The word carboxyl is a combination of two words carbonyl ($>\text{C}=\text{O}$) and hydroxyl (-OH).

CLASSIFICATION : Depending upon the number of -COOH groups they are classified as

(i) Monocarboxylic acids: containing one -COOH group

(ii) dicarboxylic acids: containing two -COOH groups and so on Fatty acids:

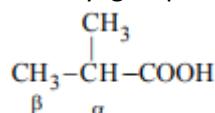
Aliphatic monocarboxylic acids are commonly called fatty acids because higher members are obtained by the hydrolysis of oils and fats.

NOMENCLATURE : There are different ways of naming carboxylic acids

(i) Common System: The common names are derived from the source of acids.

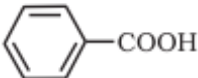
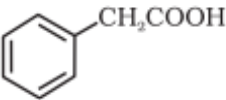
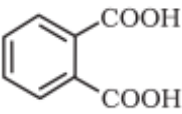
Formula	Common name	Source
HCOOH	Formic acid	Red ant (formica)
CH_3COOH	Acetic acid	Vinegar (acetium)
$\text{C}_3\text{H}_7\text{COOH}$	Butyric acid	Butter (butyrum)

The position of substituents are indicated by Greek letters α, β, γ etc. The carbon atom adjacent to carboxyl group is assigned the letter α , the next β and so on.

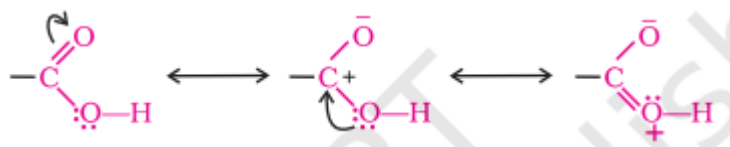


α -methyl propionic acid

(ii)

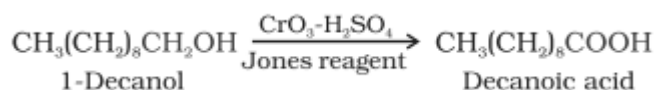
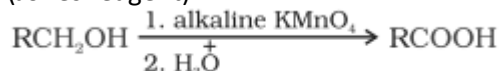
Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
$\text{HOOC-CH}_2\text{-COOH}$	Malonic acid	Propanedioic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

Structure of Carboxyl Group: In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120° . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:

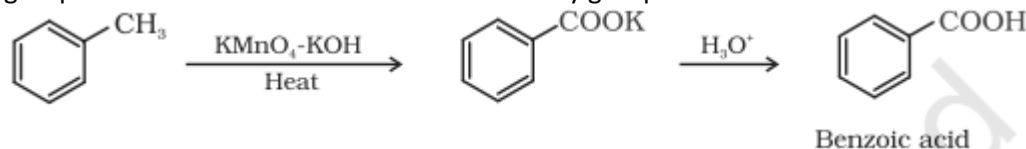


Methods of Preparation of Carboxylic Acids:

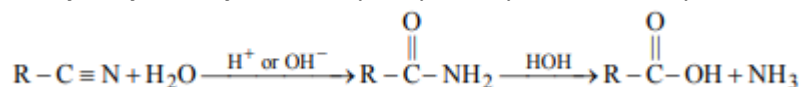
1. From primary alcohols and aldehydes : Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMnO_4) in neutral, acidic or alkaline media or by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent).



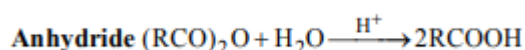
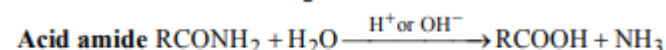
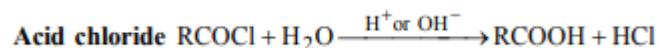
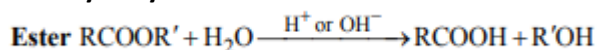
2. From alkylbenzenes : Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.



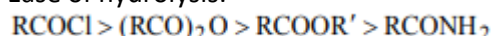
3. Hydrolysis of cyanides : Hydrolysis may be effected by acid or alkali.



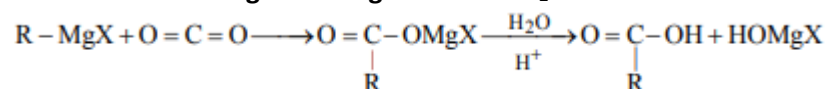
4. Hydrolysis of an Acid derivatives with alkali or acid:



Ease of hydrolysis:

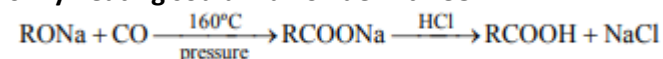


5. Reaction of Grignard Reagents with CO_2 :

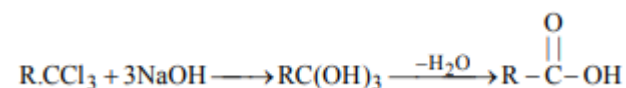


As we know, the Grignard reagents and nitriles can be prepared from alkyl are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

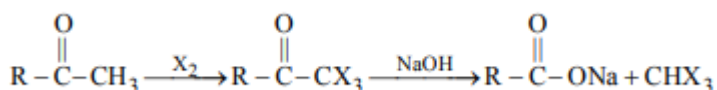
6. By heating sodium alkoxide with CO :



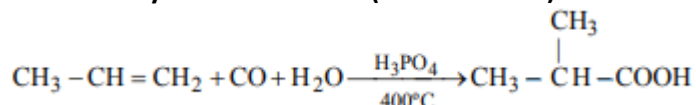
7. Hydrolysis of trihalogen derivative of alkanes:



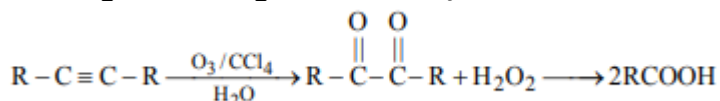
8. Oxidation of methyl ketones (Haloform reaction) with X_2/NaOH :



9. Carboxylation of alkenes (Koch reaction):

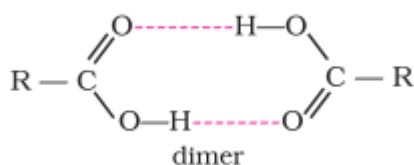


10. By ozonolysis of alkynes:

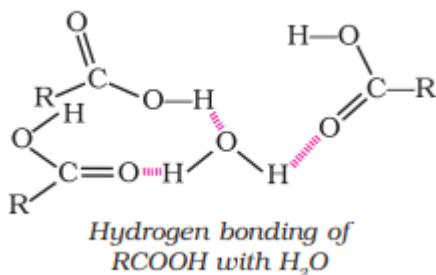


Physical Properties:

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

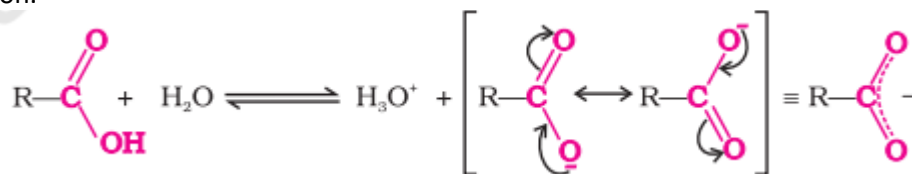


Chemical Reactions:

- Reactions Involving Cleavage of O—H Bond:

Acidity:

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



For the above reaction:

$$K_{eq} = \frac{[H_3O^+][RCOO^-]}{[H_2O][RCOOH]} \quad K_a = K_{eq} [H_2O] = \frac{[H_3O^+][RCOO^-]}{[RCOOH]}$$

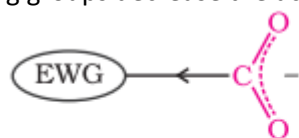
where K_{eq} is equilibrium constant and K_a is the acid dissociation constant. For convenience, the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

$$pK_a = -\log K_a$$

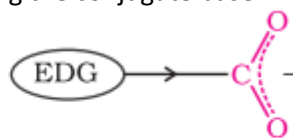
The pK_a of hydrochloric acid is -7.0 , whereas pK_a of trifluoroacetic acid (the strongest carboxylic acid), benzoic acid and acetic acid are 0.23 , 4.19 and 4.76 , respectively.

Smaller the pK_a , the stronger the acid (the better it is as a proton donor). Strong acids have pK_a values < 1 , the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15 , and extremely weak acids have pK_a values > 15 . Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols (pK_a is ~ 16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far. You already know why phenols are more acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.

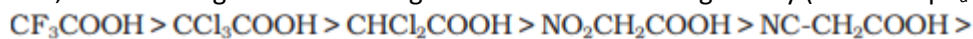


Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid

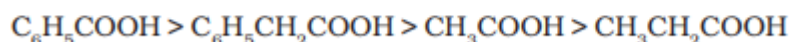


Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is $Ph < I < Br < Cl < F < CN < NO_2 < CF_3$. Thus, the following acids are arranged in order of increasing acidity (based on pK_a values):

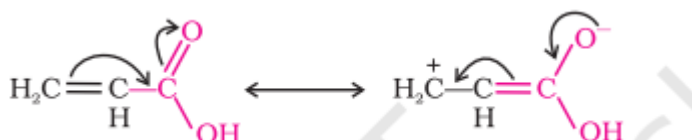


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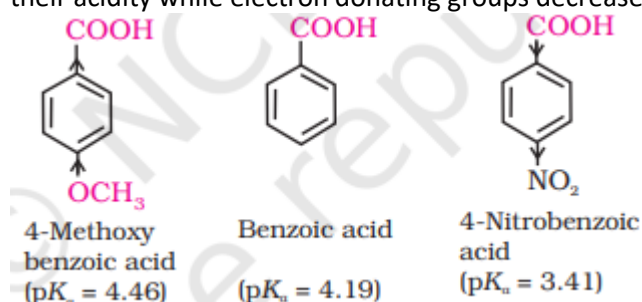
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Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:

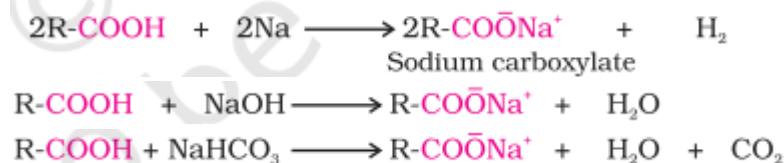


This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached.

The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

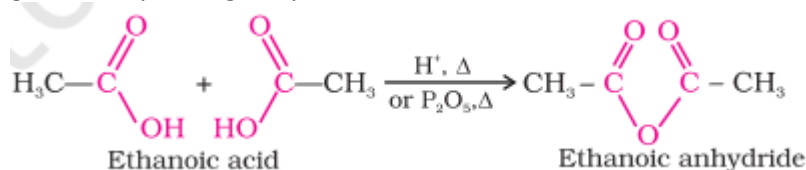


Reactions with metals and alkalis : The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalis similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.

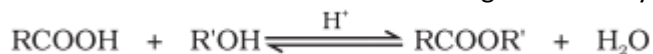


• Reactions Involving Cleavage of C–OH Bond:

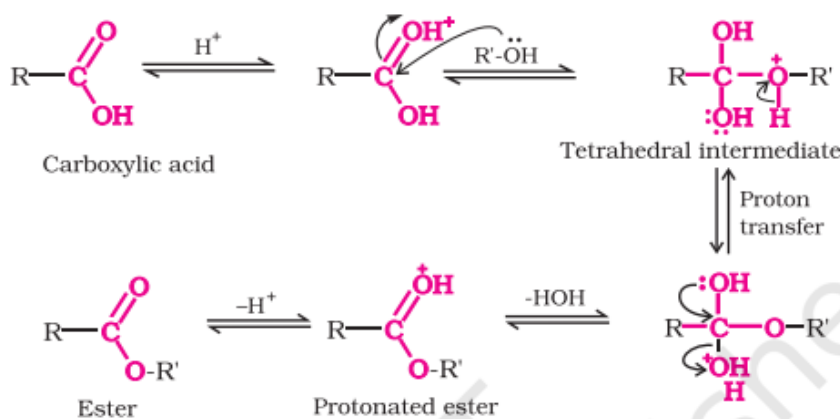
1. Formation of anhydride Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.



2. Esterification Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.



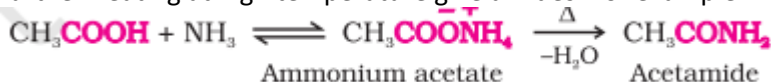
Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-OH_2^+$ group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



3. Reactions with PCl_5 , PCl_3 and SOCl_2 The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl_5 , PCl_3 or SOCl_2 . Thionyl chloride (SOCl_2) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.

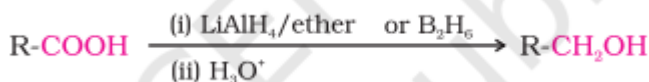


4. Reaction with ammonia Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:



• Reactions Involving $-\text{COOH}$ Group:

1. Reduction Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

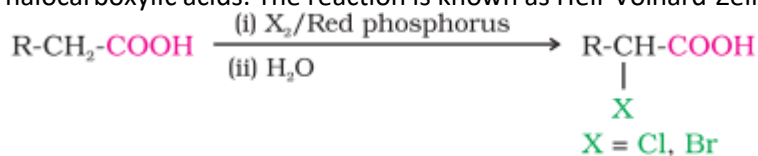


2. Decarboxylation Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.



• Substitution Reactions in the Hydrocarbon Part:

1. Halogenation: Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



α - Halocarboxylic acid

2. Ring substitution: Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo Friedel-Crafts reaction (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).

