Carboxylic Acids

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

CLASSIFICATION: Depending upon the number of —COOH groups they are classified as (i) Manocarboxylic 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

HCOOH Formic acid Red ant (formica) CH₃COOH Acetic acid Vineger (acetium)

carboxyl group is assigned the letter α , the next β and so on.

CH₃

CH₃-CH-COOH

α-methyl propionic acid

CH,CH,COOH Propionic acid Propanoic acid Butyric acid Butanoic acid CH_CH_CH_COOH Oxalic acid Ethanedioic acid HOOC-COOH HOOC -CH₂-COOH Malonic acid Propanedioic acid Benzoic acid Benzenecarboxylic acid (Benzoic acid) CH,COOH Phenylacetic acid 2-Phenylethanoic acid COOH Phthalic acid Benzene-1, 2-dicarboxylic COOH 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 Methods of Methods of Preparation PreparationPreparation of Carboxylic

(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.

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

Acid chloride $RCOCl + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + HCl$

Acid amide RCONH₂ + H₂O $\xrightarrow{H^+ \text{or OH}^-}$ RCOOH + NH₃ Anhydride (RCO)₂O+H₂O $\xrightarrow{H^+}$ 2RCOOH

Ease of hydrolysis: $RCOC1 > (RCO)_2O > RCOOR' > RCONH_2$

alkyl halides (ascending the series).

6. By heating sodium alkoxide with CO: $RONa + CO \xrightarrow{160^{\circ}C} RCOONa \xrightarrow{HCl} RCOOH + NaCl$

7. Hydrolysis of trihalogen derivative of alkanes:

 $R.CCl_3 + 3NaOH \longrightarrow RC(OH)_3 \xrightarrow{-H_2O} R - C - OH$

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

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

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.

R - C C - R

Physical Properties:

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.

For the above reaction:

phenols.

attached.

COOH

The pKa of hydrochloric acid is -7.0, where as pKa of trifluoroacetic acid (the strongest carboxylic acid), benzoic acid and acetic acid are 0.23, 4.19 and 4.76, respectively. Smaller the pKa, the stronger the acid (the better it is as a proton donor). Strong acids have

acids, weak acids have pK_a values between 5 and 15, and extremely weak acids have pKa 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

pKa values < 1, the acids with pKa values between 1 and 5 are considered to be moderately strong

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) Electron donating group (EDG) stabilises the carboxylate anion destabilises the carboxylate anion and weakens the acid and strengthens the acid The effect of the following groups in increasing acidity order is Ph < I < Br < Cl < F < CN < NO₂ < CF₃ FCH2COOH > ClCH2COOH > BrCH2COOH > HCOOH > ClCH2CH2COOH > $(continue) \leftarrow$ $\mathsf{C_6H_5COOH} > \mathsf{C_6H_5CH_2COOH} > \mathsf{CH_3COOH} > \mathsf{CH_3CH_2COOH}$ corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:

OCH₃

4-Methoxy Benzoic acid 4-Nitrobenzoic acid
$$(pK_a = 4.46)$$
 $(pK_a = 4.19)$ $(pK_a = 3.41)$

Reactions with metals and alkalies :The carboxylic acids like alcohols evolve hydrogen with

 $R\text{-COOH} + NaHCO_3 \longrightarrow R\text{-COONa}^{\dagger} + H_2O + CO_2$

their acidity while electron donating groups decrease their acidity.

COOH

 Reactions Involving Cleavage of C-OH Bond: 1. Formation of anhydride Carboxylic acids on heating with mineral acids such as H₂SO₄ or with P₂O₅ give corresponding anhydride.

2. Esterification Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral

Ethanoic anhydride

Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is neutral water molecule. The protonated ester so formed finally loses a proton to give the ester. Tetrahedral intermediate Carboxylic acid

acid such as concentrated H₂SO₄ or HCl gas as a catalyst.

RCOOH + R'OH \rightleftharpoons RCOOR' + H₂O

Ethanoic acid

Protonated ester Ester 3. Reactions with PCI₅, PCI₃ and SOCI₂ The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl₅, PCl₃ or SOCl₂. Thionyl chloride (SOCI₂) is preferred because the other two products are gaseous and escape the reaction mixture

making the purification of the products easier.
$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$
4. Reaction with ammonia Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:
$$CH_3COOH + NH_3 \Longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_4$$

$$Ammonium acetate$$
• Reactions Involving –COOH Group:

1. Reduction Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or

decarboxylation. R-COONa $\xrightarrow{\text{NaOH & CaO}}$ R-H + Na₂CO₃ Substitution Reactions in the Hydrocarbon Part:

R-COOH (i) LiAlH₄/ether or B_2H_6 \longrightarrow R-CH₂OH

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 αhalocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

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

X = Cl, Br α – Halocarboxylic acid

Friedel-Crafts reaction (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).

COOH

Conc.
$$HNO_3 +$$

Conc. H_2SO_4

(i) Common System: The common names are derived from the source of acids. Formula Common name Source C₂H₂ COOH Butyric acid Butter (butyrum) The position of substituents are indicated by Greek letters α , β , γ etc. The carbon atom adjascent to

1. From primary alcohols and aldehydes: Primary alcohols are readily oxidised to carboxylic acids

with common oxidising agents such as potassium permanganate (KMnO₄) in neutral, acidic or alkaline media or by potassium dichromate (K2Cr2O7) and chromium trioxide (CrO3) in acidic media

 $RCH_2OH \xrightarrow{1. \text{ alkaline KMnO}_4} RCOOH$ $CH_3(CH_2)_8CH_2OH \xrightarrow{CrO_3-H_2SO_4} CH_3(CH_2)_8COOH$ 1-Decapol

Decanoic acid

 $R-C \equiv N+H_2O \xrightarrow{H^+ \text{ or } OH^-} R-C-NH_2 \xrightarrow{HOH} R-C-OH+NH_3$ 4. Hydrolysis of an Acid derivatives with alkali or acid: Ester RCOOR' + $H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$

5. Reaction of Grignard Reagents with CO₂: $R - MgX + O = C = O \longrightarrow O = C - OMgX \xrightarrow{H_2O} O = C - OH + HOMgX$

8. Oxidation of methyl ketones (Haloform reaction) with X2/NaOH:

9. Carboxylation of alkenes (Koch reaction):

 $CH_3 - CH = CH_2 + CO + H_2O \xrightarrow{H_3PO_4} CH_3 - CH - COOH$ 10. By ozonolysis of alkynes:

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

dimer

Hydrogen bonding of

 $K_{eq} = \frac{[\text{H}_3\overset{+}{\text{O}}] [\text{RCOO}]}{[\text{H}_2\text{O}] [\text{RCOOH}]}$ $K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\overset{+}{\text{O}}] [\text{RCOO}]}{[\text{RCOOH}]}$ 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 pKa value rather than its Ka value. $pK_a = -\log K_a$

acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be

carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than

groups increase the acidity of carboxylic acids by stabilising the conjugate base through

of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability

 $H_2O \Longrightarrow H_3O^+ + R - C$

Thus, the following acids are arranged in order of increasing acidity (based on pK_a values): CF₃COOH > CCl₃COOH > CHCl₂COOH > NO₂CH₂COOH > NC-CH₂COOH > Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of

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

The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases

 $C-CH_3 \xrightarrow{H', \Delta} CH_3 - CCC - CH_3$

$$\begin{array}{lll} {\rm 3RCOOH} & + & {\rm PCl_3} & \longrightarrow & {\rm 3RCOCl} & + & {\rm H_3PO_3} \\ {\rm RCOOH} & + & {\rm SOCl_2} & \longrightarrow & {\rm RCOCl} & + & {\rm SO_2} & + & {\rm HCl} \\ {\rm \textbf{4. Reaction with ammonia}} & {\rm Carboxylic\ acids\ react\ with\ ammonia\ to\ give\ ammonium\ salt\ which\ on\ further\ heating\ at\ high\ temperature\ give\ amides.} & {\rm For\ example:} \\ {\rm CH_3COOH} & + & {\rm NH_3} & \Longrightarrow & {\rm CH_3COONH_4} & \xrightarrow{\Delta} & {\rm CH_3CONH_4} \\ & & {\rm Ammonium\ acetate} & \xrightarrow{-{\rm H_2O}} & {\rm Acetamide} \\ & \bullet & {\rm \textbf{Reactions\ Involving\ -COOH\ Group:}} \\ {\rm \textbf{1. Reduction\ Carboxylic\ acids\ are\ reduced\ to\ primary\ alcohols\ by\ lithium\ aluminium\ hydride\ or\ better\ with\ diborane.} & {\rm Diborane\ does\ not\ easily\ reduce\ functional\ groups\ such\ as\ ester,\ nitro,\ halo,\ etc.} \\ {\rm Sodium\ borohydride\ does\ not\ reduce\ the\ carboxyl\ group.} \end{array}$$

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

Conc.
$$HNO_3 +$$
 $Conc. H_2SO_4$
 $COOH$
 $COOH$
 $Br_2/FeBr_3$
 m -Bromobenzoic acid

 $COOH$
 $Br_2/FeBr_3$
 m -Bromobenzoic acid