(iii) Solubility.

Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this largely due to their ability to form hydrogen bonds with water molecules. The water solubility of the acids decreases as the relative molecular mass increases because the structure becomes relatively more hydrocarbon in nature and hence covalent. All carboxylic acids are soluble in organic solvents.

(3) Write two industrial preparations of carboxylic acids.

(i) From ethanol.

Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganite (II) ethanoate catalyst. Ethanal itself is obtained from ethylene.

$$HC \equiv CH \xrightarrow{\text{dil. } H_2SO_4 / HgSO_4} CH_3CHO \xrightarrow{O_2 / (CH_3COO)_2Mn} CH_3COOH.$$

(ii) From Petroleum

liquid phase air oxidation of $C_5 - C_7$ alkanes obtainable from petroleum at high temperature and pressure will give $C_5 - C_7$ carboxylic acids with methanoic, propanoic and butanedioic acids as by-products.

$$C_5 - C_7 \xrightarrow{O_2 / \text{High temperature and Pressure}} \underset{\text{Carboxylic acids}}{C_5 - C_7}$$

(4) With equations and brief explanations, discuss the synthetic preparation of carboxylic acid.

(i) Oxidation of primary alcohols and aldehydes:

Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution

$$RCH_2OH \xrightarrow{[O],\ \text{excess acid / } KMnO_4} RCHO \xrightarrow{[O]} RCOOH$$

(ii) Hydrolysis of nitriles (cyanides) or esters.

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

(R = alkyl or anyl radical)

$$RCOOR' \xrightarrow{H_2O / H^+ \text{ reflux}} RCOOH + R'OH$$

$$C_6H_5CH_2CN + 2H_2O \xrightarrow{H^+} C_6H_5CH_2COOH + NH_4^+$$

$$CH_3CH_2COOCH_3 \xrightarrow{H_2O / H^+ \text{ reflux}} CH_3CH_2COOH + CH_3OH$$

(iii) Carbonation of Grignard reagent.

Aliphatic carboxylic acids are obtained by bubbling Carbon (IV) oxide into the Grignard reagent and then hydrolyzed with dilute acid.

$$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} RCOOMgBr \xrightarrow{H_2O / \text{dil. acid}} RCOOH + MgBrOH$$

R may be 1°, 2°, 3° aliphatic alkyl or aryl radical.

In the preparation of benzoic acid, the reagent is added to solid Carbon (IV) oxide (dry ice) which also serves as coolant to the reaction mixture.

$$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_5H_6COOH + MgBrOH$$

(5) With Chemical equations only; outline the reduction, decarboxylation and esterification of carboxylic acid.

CHEMICAL REACTIONS.

(I) Reduction of Primary alcohol

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

$$(RCH_2O)_4AlLi \xrightarrow{4H_2O} 4RCH_2OH + Al(OH)_3 + LiOH$$

$$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

Butanoic acid. Butanol

(II) Decarboxylation.

$$CH_3CH_2CH_2COONa + NaOH \xrightarrow{fuse} CH_3CH_2CH_3 + Na_2CO_3$$

Kolbe synthesis

$$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis / aq. } CH_3OH} CH_3(CH_2)_2CH_3 + CO_2 \text{ (anode)} + 2NaOH + H_2 \text{ (cathode)}$$

(III) Esterification.

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \overset{H^+}{\rightleftharpoons} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$$

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ASSIGNMENT ON CARBOXYLIC ACIDS.

(1) Give the IUPAC names of the following compounds.

$HCOOH$ ⇒ Methanoic acid.

$HOOCCH_2CH_2CH_2COOH$ ⇒ Pentan-1,5-dioc acid

$CH_3CH_2CH_2COOH$ ⇒ Butanoic acid

HO_2C-CO_2H ⇒ Ethanedioc acid

$CH_3(CH_2)_4COOH$ ⇒ Hexanoic acid

$CH_3CH=CHCH_2CH_2COOH$ ⇒ Hex-4-eneoic acid.

(2) Discuss briefly the physical properties of Carboxylic acids under the following headings
(i) physical appearance (ii) Boiling point (iii) Solubility

(I) Physical appearances.
All simple aliphatic Carboxylic acids upto C_{10} are liquids at room temperature. Most other Carboxylic acids are solid at room temperature although anhydrous Carboxylic acid (Acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature.

(II) Boiling Points.
Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher melting points than their aliphatic counterparts of comparable relative molecular mass.