CHM 102

Carboxylic Compounds

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1) Give the IUPAC names of the following compounds

a) $HCOOH$ ⟶ Methanoic acid

b) $HOOCCH_2CH_2CH_2COOH$ ⟶ pentan-1,5-dioic acid

c) $CH_3CH_2CH_2COOH$ ⟶ Butanoic acid

d) HO_2C-CO_2H ⟶ Ethanedioic acid

e) $CH_3(CH_2)_4COOH$ ⟶ Hexanoic acid

f) $CH_3CH=CHCH_2CH_2COOH$ ⟶ Hex-4-enoic acid

2) Discuss briefly the physical properties of carboxylic acids under the following headings

(i) physical appearance

All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature although anhydrous carboxylic acid (ethanoic acid) also known as glacial ethanoic acid freezes to an ice-like solid below room temperature.

(2) Boiling Point

This increases with increasing relative molecular mass.

Aromatic carboxylic acids are crystalline solids and have higher melting than their aliphatic counterparts of comparable relative molecular mass.

3) Solubility

Lower molecular mass carboxylic acids with up to four carbon atom in their molecules are soluble in water. this largely due to their ability to form hydrogen bonds with water molecules.

3) Industrial preparation of carboxylic acids

(a) From ethanal

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

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

(b) From petroleum

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

$C_5 - C_7$ Cl_2/high temp and pressure $C_5 - C_7$ Carboxylic acid

4) With Equation and brief explanation discuss the synthetic properties of Carboxylic acid.

- Hydrolysis of nitriles (cyanides) or esters

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

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

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

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

where R = alkyl or aryl radical.

5) With chemical equation only, outline the reduction, decarboxylation and esterification of Carboxylic acid.

Reduction

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4Al + 2LiAlO_2 + 4H_2$

$\downarrow$

$4RCH_2OH + Al(OH)_3 + LiOH$

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH$

$\downarrow H^+$

$CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$

Decarboxylation

$CH_3CH_2CH_2COONa + NaOH$

↓ fuse

$CH_3CH_2CH_3 + Na_2CO_3$

$2CH_3CH_2COONa + 2H_2O$

↓ electrolysis / aq. CH_3OH

$CH_3(CH_2)CH_3 + \underset{(anode)}{CO_2} + 2NaOH + \underset{(cathode)}{H_2}$