NAME - MARKMANUEL AGBEZIBE MARKBERE WINNER

DEPT - MECHANICAL ENGINEERING

MATRIC NO - 19/ENG06/035

CHEM 102: GENERAL CHEMISTRY II

Assignment

1. Give the IUPAC names of the following compounds

HCOOH HOOCCH₂CH₂COOH

CH₃CH₂COOH HO₂C-CO₂H

CH₃(CH₂)₄COOH CH₃CH=CHCH₂COOH

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

i. Physical appearance ii. Boiling point iii. Solubility

- 3. Write two industrial preparations of carboxylic acids
- 4. With equations and brief explanation discuss the synthetic preparation of carboxylic acid
- 5. With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid

ANSWERS

1. HCOOH - Methanoic acid

HOOCCH₂CH₂CH₂COOH - Pentan-1,5-dioic acid

CH₃CH₂COOH - Butanoic acid

HO₂C-CO₂H - Ethanedioic acid

CH₃(CH₂)₄COOH - Hexanoic acid

CH₃CH=CHCH₂CH₂COOH - Hex-4-eneoic acid

2.

Physical appearancesAll simple aliphatic carboxylic acids up to C₁₀ 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.

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. Industrial preparations of carboxylic acids

a. From Carbon(II) oxide

Methanoic acid (formic acid) is manufactured by adding carbon(II)oxide under pressure to hot aqueous solution of sodium hydroxide. The free carboxylic acid is liberated by careful reaction with tetraoxosulphate (vi) acid (H₂SO₄)

CO
$$\rightarrow$$
 HCOONa \rightarrow HCOOH + NaHSO₄

b. From ethanal

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

$$HC \equiv CH \frac{-dil. H_2SO_4/HgSO_4}{CH_3COO} CH_3CHO \frac{-O_2/(CH_3COO)_2M_{\odot}}{CH_3COOH}$$

c. 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.

- 4. Synthetic preparation of carboxylic acid
 - a. 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

b. Carbonation of Grignard reagent

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

$$RMgBr + CO_2 (C_2H_5)_2O \longrightarrow RCOOMgBrH_2O/dil. acid RCOOH + MgBrOH$$

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

$$C_6H_5MgBr + CO_2 - (C_2H_5)_2O \rightarrow C_6H_5COOMgBr - H_2O/H^+ \rightarrow C_6H_5COOH + MgBrOH$$

c. Hydrolysis of nitriles (cyanides) or esters

$$RCN + 2H_2O \longrightarrow H^+ \rightarrow RCOOH + NH_4^+$$

(R=alkyl or aryl radical)

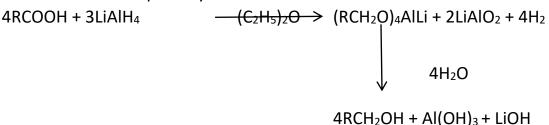
RCOOR'
$$H_2O/H^+$$
 reflux \rightarrow RCOOH + R'OH

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

$$CH_3CH_2COOCH_3$$
 $H_2O/H^+reflux$ > $CH_3CH_2COOH + CH_3OH$

5.

a. Reduction to primary alcohol



b. Decarboxylation

Kolbe synthesis

 $H_{2(cathode)}$

c. Esterification

$$\mathsf{CH_3CH_2COO} + \mathsf{CH_3CH_2CH_2OH} \xleftarrow{\mathsf{H}^+} \mathsf{CH_3CH_2CH_2COO} \ \mathsf{CH_2CH_2CH_3} + \mathsf{H_2O}.$$