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DEPARTMENT: MEDICAL LABOURATORY SCIENCE

COURSE TITLE: GENERAL CHEMISTRY II

COURSE CODE: CHM 102

ASSIGNMENT TITLE: ASSIGNMENT ON CARBOXYLIC ACID

ANSWERS

1. a. HCOOH - Methanoic acid

b. HOOCCH₂CH₂CH₂COOH - Pentan-1,5-dioic acid

c. CH₃CH₂CH₂COOH - Butanoic acid

d. HO₂C-CO₂H - Ethanedioic acid

e. CH₃(CH₂)₄COOH – Hexanoic acid

f. CH₃CH=CHCH₂CH₂COOH - Hex-4-eneoic acid

2. PROPERTIES

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 (acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature.

II. BOILING POINT

Boiling point increases with increasing relative molecular mass. Aromatic 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. INDUSTRAIL PREPARATION

I. 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)

NaOH
$$H_2SO_4$$
 CO \rightarrow HCOONa \rightarrow HCOOH + NaHSO $_4$

II. FROM ETHANOL

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

Dil.
$$H_2SO_4/HgSO_4$$
 $O_2/(CH_3COO)_2Mn$ $HC \equiv CH$ \rightarrow CH_3CHO \rightarrow CH_3COOH

4. SYNTHETIC PREPARATION

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. K₂Cr₂O₇ or KMnO₄) in acidic solution

[O], excess acid/KMnO₄ [O]
$$RCH_2OH \qquad \rightarrow \qquad RCHO \quad \rightarrow \qquad RCOOH$$

II. HYDROLYSIS OF NITRILES (CYANIDES) OR ESTERS

$$H^{\dagger}$$
 RCN + $2H_2O \rightarrow RCOOH + NH_4^{\dagger}$ (R=alkyl or aryl radical)

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

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

$$H_2O/H^{\dagger}$$
 reflux
CH₃CH₂COOCH₃ \rightarrow CH₃CH₂COOH + CH₃OH

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

$$(C_2H_5)_2O$$
 $H_2O/dil. acid$ $RMgBr + CO_2 \rightarrow RCOOMgBr \rightarrow RCOOH + MgBrOH$

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

$$(C_2H_5)_2O$$
 H_2O/H^+

5. REDUCTION TO PRIMARY ALCOHOL

 $(C_2H_5)_2O$

$$4RCOOH + 3LiAlH_4 \rightarrow (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

↓4H₂O

$$4RCH2OH + Al(OH)3 + LiOH$$

LiAlH₄

 $CH_3CH_2COOH \rightarrow CH_3CH_2CH_2OH$

Butanoic acid Butanol

DECARBOXYLATION

fuse

CH₃CH₂COONa + NaOH → CH₃CH₂CH₃ + Na₂CO₃

Kolbe synthesis

Electrolysis/aq. CH₃OH

 $2CH_3CH_2COONa + 2H_2O \rightarrow CH_3(CH_2)_2CH_3 + CO_{2(anode)} + 2NaOH + H_{2(cathode)}$

ESTERIFICATION

 H^{\dagger}

 $CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \leftrightarrow CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$