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DEPARTMENT: GEOLOGY

CHM 102 ASSIGNMENT

ASSIGNMENT ON CARBOXYLIC ACID

1. Give the IUPAC names of the following compounds

i) $HCOOH$

ii) $HOOCCH_2CH_2CH_2COOH$

iii) $CH_3CH_2CH_2COOH$

iv) HO_2C-CO_2H

v) $CH_3(CH_2)_4COOH$

vi) $CH_3CH=CHCH_2CH_2COOH$

Answers.

	Organic Compounds	IUPAC names
i	$HCOOH$	Methanoic acid
ii	$HOOCCH_2CH_2CH_2COOH$	Pentan-1,5-dioic acid
iii	$CH_3CH_2CH_2COOH$	Butanoic acid
iv	HO_2C-CO_2H	Ethanedioic acid
v	$CH_3(CH_2)_4COOH$	Hexanoic acid
vi	$CH_3CH=CHCH_2CH_2COOH$	Hex-4-enoic acid

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

i) Physical appearance ii) Boiling point iii) Solubility.

Answers

A PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

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 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 largerly 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 water.

3. Write two industrial preparations of carboxylic acids.

Answers.

INDUSTRIAL PREPARATIONS OF CARBOXYLIC ACIDS

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 (H_2SO_4)

$$CO \xrightarrow{NaOH} HCOONa \xrightarrow{H_2SO_4} HCOOH + NaHSO_4$$

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:

$$C_5 - C_7 \xrightarrow{O_2/\text{High temperature and pressure}} C_5 - C_7 \text{ carboxylic acids}$$

($C_5 - C_7$ alkanes)

4 With equations and brief explanation discuss the synthetic preparation of carboxylic acid.

SYNTHETIC PREPARATION OF CARBOXYLIC ACID.

1 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 $K_2Cr_2O_7$ (potassium dichromate (VI)) or $KMnO_4$ (potassium manganate (VII)) in acidic solution.

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

Example: OXIDATION OF ETHANOL TO ETHANOIC ACID

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$
$$CH_3CHO + [O] \longrightarrow CH_3COOH$$

2. CARBONATION OF GRIGNARD REAGENT

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

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

N/B: R may be 1°, 2°, 3° aliphatic alkyl or aryl radical.

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

$$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$$

3 HYDROLYSIS OF NITRILES (CYANIDES) or ESTERS.

Nitriles undergo hydrolysis to form amides. The amides further undergo reaction in the presence of a catalyst which then to form

carboxylic acids. The catalyst for this reaction is H^+ or OH^-. Furthermore, application of mild reaction condition helps in ceasing the reaction in the amide stage.

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

(R = alkyl or aryl radical)

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

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

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

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

CHEMICAL REACTIONS

1. REDUCTION TO PRIMARY ALCOHOL

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

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

$$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

2. DECARBOXYLATION

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

Kolbe synthesis

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

3 ESTERIFICATION

$$CH_3CH_2CH_2COOH + CH_2CH_2CH_2OH \xleftrightarrow{H^+} CH_3CH_2CH_2COOCH_2CH_2 + H_2O$$