IN DEPTH

15. Carboxylic acids and derivatives

An organic compound A has the molecular formula $C_5H_{10}O_2$.

1. Hydrolysis of A gives a saturated monocarboxylic acid B and a saturated monoalcohol C. The acid B reacts with phosphorus pentachloride to give a compound D. By the action of an excess of sodium ethanoate on D, we obtain NaCℓ and an organic compound E with a saturated carbon chain, of molar molecular mass : $M = 102\ g.mol^{-1}$.
   - 1.1. Specify the chemical functional groups of A, D and E.
   - 1.2. Show that the molecular formula of E is $C_4H_6O_3$.

   Given : $H = 1$; $C = 12$ $O = 16\ g.mol^{-1}$
   - 1.3. Give the condensed structural formulas and the names of E, D and B.

2. Alcohol C is oxidized by a solution of potassium dichromate in an acidic medium. An organic compound F is formed giving a yellow precipitate with 2.4-dinitrophenyl hydrazine (D.N.P.H) but does not react with the Fehling solution.
   - 2.1. What is the chemical functional group of F? Justify.
   - 2.2. Identify C and F.
   - 2.3. Deduce the condensed structural formula of A and give its name.

16. Butanoic acid

Butanoic acid, also known as butyric acid, is a fatty carboxylic acid used in the preparation of soap. It is proposed in this exercise to study its properties.

1. **Determination of the molecular formula of butanoic acid**
   - 1.1. Write the general molecular formula of a saturated linear chain monocarboxylic acid showing the acid functional group.
   - 1.2. One of these acids is reacted with phosphorus pentachloride ; we get a non-branched organic compound B with a molar mass of $106.5\ g.mol^{-1}$.
     - 1.2.1. Write the equation of the reaction.
     - 1.2.2. Indicate the family of compound B ; give its general molecular formula.
     - 1.2.3. Determine the molecular formula of B.

     Given : $H = 1$; $C = 12$; $O = 16$ and $C\ell = 35.5\ g.mol^{-1}$
     - 1.2.4. Identify B.
     - 1.2.5. Verify that the acid A from which B is derived is butanoic acid.

2. **Study of some properties of butanoic acid**

The series of the following reactions are carried out according to the appropriate experimental conditions with butanoic acid :

$$C \longrightarrow A\,(1)$$

$$A + C \rightleftarrows E + H_2O\,(2)$$

$$2A \longrightarrow D + H_2O\,(3)$$

2.1. Name the reaction (1) and identify C.
2.2. Give 3 characteristics of the reaction (2) and identify E.
2.3. Identify D, and write the equation of reaction (3).

17. Importance and Characteristics of the Ester

Two skiers broke their legs in Faraya during a ski session. These two skiers underwent two surgeries at two different hospitals. In the first case the leg was treated with a metal screw, while in the second case it was treated with a screw formed of the ester-based polymers.

Three months later the patient in the first case was subjected to a second surgery to remove the metal screw while in the second case the ester-based screw was completely resorbed and no need for further surgery. Among the many constituents of this ester-based screw, we note the presence of an ester (X) which will be the objective of our study.

1. **Characteristics of the disappearance reaction of the ester (X)**

1.1. Give the general molecular formula of an ester in terms of R and R'. (R, R' = alkyl group or hydrogen atom).

1.2. Knowing that human blood is very rich in water, explain the fact of the disappearance of the ester-based screw in the body in the second case.

1.3. Write the equation of the reaction of the disappearance of the ester in terms of R and R'.

1.4. What characteristic can be given to this reaction on the basis of the text?

1.5. Give two other characteristics of this reaction.

2. **Identification of the products (A) and (B)**

Propose that the products resulting from such a reaction are a carboxylic acid (A) of the general formula $C_nH_{2n}O_2$ and a monoalcohol (B) of the formula C_3H_8O.

2.1. Determine the molecular formula of (A) given that the mass percentage of oxygen is 36.36 %. Deduce its condensed structural formula knowing that the carbon chain is non-branched and acyclic.

2.2. To identify the monoalcohol (B) it is treated with an acidified solution of potassium permanganate $KMnO_4$, a product (C) is formed which gives a yellow-orange precipitate with DNPH but with no reaction with the Schiff's reagent.

2.2.1. What is the nature of the product (C) thus formed? Deduce the class of alcohol (B).

2.2.2. Give the condensed structural formulas and names of the alcohol (B) and the product (C).

2.3. Give the condensed structural formula and the name of the ester (X).

3. Experimental study

Density of alcohol (B) :
$d = 0.80$ g.cm^{-3}.
$M_C = 12$ g.mol^{-1} $M_H = 1$ g.mol^{-1} $M_O = 16$ g.mol^{-1}

Document 1

A volume $V_B = 1.5$ mL of the alcohol (B) and a mass $m_A = 1.76$ g of the acid (A) are mixed with a few mL of concentrated sulfuric acid. The ester (X) begins to form and after a certain time the amount of the ester becomes invariable and the amount of the remaining acid is found to be 0.8×10^{-2} mol.

3.1. Determine the molar composition of the constituents at equilibrium.
3.2. Determine the yield of this esterification reaction.
3.3. How the amount of the formed ester varies if the temperature is increased. Justify.
3.4. The carboxylic acid (A) is replaced by its chlorinated derivative (D) :
3.4.1. Write the equation of the new esterification reaction.
3.4.2. Give the characteristics of this reaction.

18. Carboxylic acids and derivatives

Carboxylic acids and their derivatives are widely used in the paint, textile, pharmaceutical industry...etc.

Consider a saturated carbon chain carboxylic acid (A) of formula R - COOH.

R being an alkyl radical of formula C_nH_{2n+1}.
$M_C = 12$ g.mol^{-1} $M_H = 1$ g.mol^{-1} $M_O = 16$ g.mol^{-1}

Document 1

1. Identification of an Acid A

A mass of 2.64 g of the carboxylic acid (A) is converted completely to its derivative (B) by reacting (A) with thionyl chloride $SOC\ell_2$. The compound (B) is isolated and weighed, its mass is found to be 3.195 g.

1.1. Indicate the functional group of (B).
1.2. Write the equation of the reaction leading from (A) to (B) using the general molecular formulas of the organic compounds.
1.3. By referring to **document 1**, determine the molecular formula of the acid (A). Deduce that of (B).
1.4. Write the possible condensed structural formulas of (A) and (B).
1.5. Name (A) and (B), consider that their carbon chains are non-branched.

2. Preparation of an acid anhydride from (A)

Intermolecular dehydration of the acid (A) in the presence of P_2O_5 and at 700 °C leads to the anhydride (C).

2.1. Write the equation of the dehydration reaction of the acid (A) leading to (C).
2.2. Name the product (C).
2.3. In the synthesis of the anhydride (C) it is necessary to operate in a dry and clean beaker. Justify why.

3. Preparation of an ester from (A)

Pineapple is probably the most emblematic of tropical fruits. Its unique perfume and its green crown have earned it, in many countries, the nickname "King of the Fruits". The aroma of pineapple is due to an ester (E) named ethylbutanoate.

Density of alcohol : $d = 0.8\ g.cm^{-3}$.
In the case of an equimolar mixture of a carboxylic acid and a primary alcohol, the yield of the esterification reaction is 66 %.

Document 2

2.64 g of the acid (A) are reacted with 1.725 mL of the alcohol in the presence of a few drops of concentrated sulfuric acid and then the mixture is heated at 100 °C. for a few hours.

3.1. Identify the alcohol used in the synthesis of the ester (E).
3.2. Write, using the condensed structural formulas, the equation of the synthesis reaction of (E).
3.3. Calculate the initial number of moles of used (A) and alcohol.
3.4. The remaining acid (A) is titrated with a 1 $mol.L^{-1}$ of sodium hydroxide NaOH solution. Equivalence is reached when the added volume of the base is equal to15 mL.
3.4.1. Write the equation of the titration reaction.
3.4.2. Determine the amount of acid remaining.
3.4.3. Deduce the yield of this esterification.
3.4.4. Verify by referring to **document 2**, whether the chemical equilibrium is reached or not.
3.4.5. Pick out from **document 2** a characteristic of the esterification reaction.

19. Analysis and synthesis of an organic compound (X)

An organic compound (X) has the molecular formula $C_5H_{10}O_2$. Hydrolysis of (X) gives a carboxylic acid (A) and an alcohol (B). The acid (A) reacts with $PC\ell_5$ phosphorus pentachloride to give an organic compound (C).

1. Identification of (X)

The mild oxidation of the alcohol (B) leads to a compound (D) which reacts with DNPH but does not react with the Schiff's reagent.

1.1. Specify the chemical organic family of compound (X).
1.2. Deduce the chemical organic family of (D) as well as that of (B).
1.3. Write the possible condensed structural formulas of (B) and (D).

1.4. Quantitative analysis of the acid (A) shows that it is formed of 2 carbon atoms.
1.4.1. Identify the acid (A).
1.4.2. Deduce the condensed structural formula and the name of the compound (X).
1.5. Identify the organic compound (C).

2. Different methods of synthesis of compound (X)

The synthesis of the compound (X) can be carried out either directly or indirectly.

In the case of an equimolar mixture of a carboxylic acid and a secondary alcohol, the yield of the esterification reaction is 60 %.
Concentrated sulfuric acid becomes a dehydrating agent if used in large quantities.

Document 1

2.1. Direct method of synthesis

We mix 0.2 mol of the acid (A) with 0.1 mol of the alcohol (B). A few drops of concentrated sulfuric acid are added and the mixture is heated at reflux for a few hours. Once equilibrium is reached, 0.08 mol of the compound (X) is recovered.

2.1.1. Determine the amount of each constituent at equilibrium.
2.1.2. Deduce the yield of the reaction.
2.1.3. Justify why the yield exceeded 60 %.
2.1.4. Explain the effect of using a small amount of concentrated sulfuric acid and the effect of using a large amount of sulfuric acid.
2.1.5. Indicate the importance of reflux heating. Justify.
2.1.6. Indicate the 3 characteristics of the direct synthesis method.

2.2. Indirect method of synthesis :

To synthesize (X) in an indirect way, one of the 2 derivatives of (A) is used.

2.2.1. Identify these 2 derivatives.
2.2.2. Write the 2 synthesis equations of (X) from each derivative.
2.2.3. If 0.2 mol of the chlorinated derivative and 0.1 mol of the alcohol (B) are used. Determine the amount of (X) obtained in this case.
2.2.4. Why is it necessary to operate with clean and dry beakers when using the acid derivatives (A)
2.2.5. Indicate the 3 characteristics of the indirect method of synthesis.