Chapter: 5
Alcohols

Chapter Review:

1) Introduction

A straight chain mono saturated alcohol contains the hydroxyl functional group. It is represented by the general formula ROH. The general molecular formula for a mono alcohol is $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.

Naming of alcohols

Alkan~~e~~ → x-Alkanol

Number of carbon-atom	Molecular formula	Name
n = 1	CH_3OH	methanol
n = 2	C_2H_5OH	Ethanol
n = 3	C_3H_7OH	x-propanol
n = 4	C_4H_9OH	x-butanol
n = 5	$C_5H_{11}OH$	x-pentanol
n = 6	$C_6H_{13}OH$	x-hexanol

Exercise: 1

Give the IUPAC name of each of the following alcohols.

1) $CH_3 – CH_2 – CH_2 – CH_2 – OH$

1- butanol

2)
```
                    CH3
                     |
CH3 – CH  –  C  – CH2 – CH3
       |     |
      OH    CH3
```

3,3- dimethyl-2-pentanol

3)
```
CH3 – CH – (CH2)2 – CH – CH3
       |             |
      C2H5          OH
```

4)
```
          CH3
           |
CH3 – C – CH – CH2 – CH3
      |    |
     OH   C2H5
```

5- methyl-2-heptanol

3- ethyl-2- methyl-2- pentanol

5) $$\begin{array}{ccccccccc} & & CH_3 & & & & CH_3 & & \\ & & | & & & & | & & \\ CH_3 & - & C & - & CH & - & CH_2 & - & C & - & CH_3 \\ & & | & & | & & & & | & & \\ & & CH_3 & & C_2H_5 & & & & OH & & \end{array}$$

4- ethyl-2,5,5- trimethyl-2- hexanol

Exercise: 2

Write the condensed structural formula of the following alcohols.

1) 1- propanol **2) 2- pentanol**

$CH_3 - CH_2 - CH_2 - OHCH_3 - CHOH - CH_2 - CH_2 - CH_3$

3)2-methyl-2-butanol

$$\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ CH_3 & - & C & - & CH_2 & - & CH_3 \\ & & | & & & & \\ & & OH & & & & \end{array}$$

4)2,2-dimethyl-1-butanol

$$\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ CH_2 & - & C & - & CH_2 & - & CH_3 \\ | & & | & & & & \\ OH & & CH_3 & & & & \end{array}$$

5) 3- ethyl-2,2,3-trimethyl-1-pentanol

$$\begin{array}{ccccccccc} & & CH_3 & & CH_3 & & & & \\ & & | & & | & & & & \\ CH_2 & - & C & - & C & - & CH_2 & - & CH_3 \\ | & & | & & | & & & & \\ OH & & CH_3 & & C_2H_5 & & & & \end{array}$$

2) Classes of alcohol:

Alcohols are classified into three classes:

Primary alcohol (1º- alc)

$$\begin{array}{c} H \\ | \\ R - C - OH \\ | \\ H \end{array} \quad \text{or } RCH_2OH$$

Secondary Alcohol (2º –alc)

$$\begin{array}{c} R' \\ | \\ R - C - OH \\ | \\ H \end{array} \quad \text{or } RR'CHOH$$

Tertiary alcohol (3º- alc)

$$\begin{array}{c} R' \\ | \\ R - C - OH \\ | \\ R'' \end{array} \quad \text{or } RR'R''COH$$

Exercise: 3

Indicate the name and the class of the following alcohols.

1)

$$\begin{array}{ccccccccc} & & CH_3 & & CH_3 & & & & \\ & & | & & | & & & & \\ CH_2 & - & C & - & C & - & CH_2 & - & CH_3 \\ | & & | & & | & & & & \\ OH & & CH_3 & & C_2H_5 & & & & \end{array}$$

2)

$$\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ CH_3 & - & C & - & CH_2 & - & CH_3 \\ & & | & & & & \\ & & OH & & & & \end{array}$$

3)

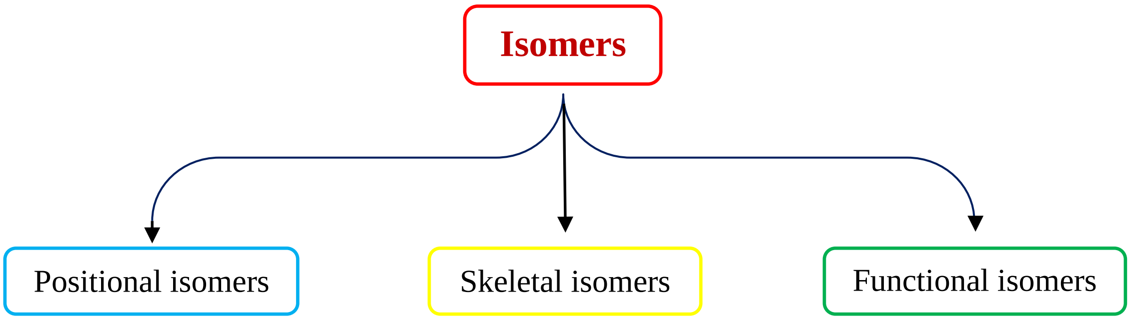
$$\begin{array}{ccccccccccc} & & CH_3 & & & & & & CH_3 & & \\ & & | & & & & & & | & & \\ CH_3 & - & C & - & CH & - & CH_2 & - & C & - & CH_3 \\ & & | & & | & & & & | & & \\ & & CH_3 & & C_2H_5 & & & & OH & & \end{array}$$

4)

$$\begin{array}{ccccccccc} CH_3 & - & CH & - & (CH_2)_2 & - & CH & - & CH_3 \\ & & | & & & & | & & \\ & & C_2H_5 & & & & OH & & \end{array}$$

3) Isomers:

Compounds that have same molecular formula but different structural formula.



Example:1

Write the condensed structural formula of all possible isomers of $C_4H_{10}O$. Give their names.

(A): $CH_3 - CH_2 - CH_2 - CH_2 - OH$ — **1 – butanol**

(B): $CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3$ — **2 – butanol**

(C): $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - OH$ — **2 – methyl – 1 – propanol**

(D): $CH_3 - \overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - CH_3$ — **2 – methyl – 2 – propanol**

(A) and (B) are positional isomers(A) and (C) are skeletal isomers

Note:

Alcohol and ether are functional isomers, since they have same molecular formula but different functional group.

Ether: R – $\boxed{O}$ – R ether group

Alcohol: R – $\boxed{OH}$ hydroxyl group

$CH_3 - CH_2 - O - CH_2 - CH_3$ and $CH_3 - CH_2 - CH_2 - CH_2 - OH$

Example:2

Write the condensed structural formula of all possible isomers of the alcohol $C_5H_{10}O$

Isomers of $C_5H_{12}O$

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$ 1-pentanol

$$\begin{array}{ccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH & - & CH_3 \\ &&&&&& | && \\ &&&&&& OH && \end{array}$$

2-pentanol

$$\begin{array}{ccccccccc} CH_3 & - & CH_2 & - & CH & - & CH_2 & - & CH_3 \\ &&&& | &&&& \\ &&&& OH &&&& \end{array}$$

3-pentanol

2-methyl-1-butanol

$$\begin{array}{ccccccccc} CH_3 & - & CH_2 & - & CH & - & CH_2 & - & OH \\ &&&& | &&&& \\ &&&& CH_3 &&&& \end{array}$$

3-methyl-1-butanol

$$\begin{array}{ccccccccc} CH_3 & - & CH & - & CH_2 & - & CH_2 & - & OH \\ && | &&&&&& \\ && CH_3 &&&&&& \end{array}$$

2-methyl-2-butanol

$$\begin{array}{ccccccc} &&&& CH_3 && \\ &&&& | && \\ CH_3 & - & CH_2 & - & C & - & CH_3 \\ &&&& | && \\ &&&& OH && \end{array}$$

3-methyl-2-butanol

$$\begin{array}{ccccccc} CH_3 & - & CH & - & CH & - & CH_3 \\ && | && | && \\ && CH_3 && OH && \end{array}$$

$$\begin{array}{ccccccc} && CH_3 &&&& \\ && | &&&& \\ CH_3 & - & C & - & CH_2 & - & OH \\ && | &&&& \\ && CH_3 &&&& \end{array}$$

2,2-dimethyl-1-propanol

4) Reactions of Alcohols

A- Mild oxidation of an Alcohol

Mild oxidationis a reaction which takes place**without breaking the carbon chain.Mild oxidation of alcohols can be carried out in three ways:**

i- Catalytic oxidation in presence of oxygen gas

ii- Catalytic dehydrogenation in the absence of oxygen gas

iii-Oxidation by oxidants ($KMnO_4$, $K_2Cr_2O_7$).


Dear students
I advice you to study the
map well

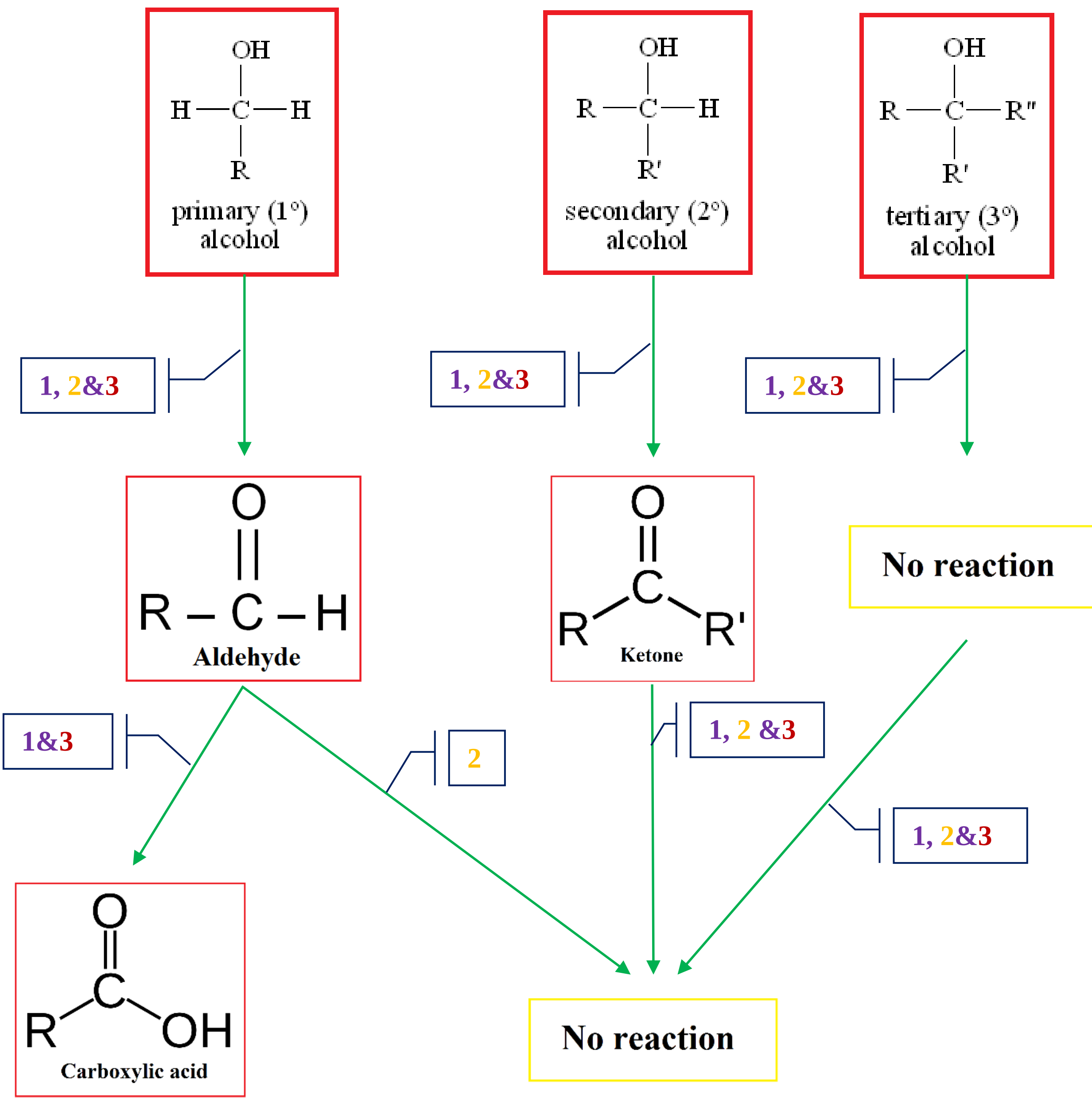
In General

Mild oxidation

(1) Catalytic oxidation (presence of oxygen)

(2) Catalytic dehydrogenation (absence of oxygen)

(3) Adding an oxidant ($KMnO_4$, $K_2Cr_2O_7$, …)



i- Catalytic oxidation in presence of oxygen

1^0 Alcohol: $RCH_2OH + \frac{1}{2} O_2 \xrightarrow[\Delta]{Cu} R-\overset{\overset{O}{||}}{C}-H$ (aldehyde) $+ H_2O$

Continous mild oxidation

$RCH_2OH + O_2 \xrightarrow[\Delta]{Cu} R-\overset{\overset{O}{||}}{C}-OH$ (carboxylic acid) $+ H_2O$

2^0 Alcohol: $R-\underset{\underset{OH}{|}}{CH}-R' + \frac{1}{2} O_2 \xrightarrow[\Delta]{Cu} R-\overset{\overset{O}{||}}{C}-R'$ (Ketone) $+ H_2O$

3^0 Alcohols don't undergo catalytic oxidation in presence of O_2.

Example:1

1- butanol + ½ O_2

$$CH_3CH_2CH_2CH_2OH + \frac{1}{2} O_2 \xrightarrow[\Delta]{Cu} CH_3CH_2CH_2-\overset{\overset{O}{||}}{C}-H + H_2O$$

butanal

2- butanol + ½ O_2

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 + \frac{1}{2} O_2 \xrightarrow[\Delta]{Cu} CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 + H_2O$$

butanone

Example:2

2- butanol + ½ O_2

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 + \frac{1}{2} O_2 \xrightarrow[\Delta]{Cu} CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 + H_2O$$

butanone

ii- Catalytic dehydrogenation in absence of oxygen

1^0 Alcohol: $RCH_2OH \xrightarrow[300^0C]{Cu} R-\overset{\overset{O}{||}}{C}-H$ (Aldehyde) $+ H_2$

2^0Alcohol: $R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[300^0C]{Cu} R-\overset{\overset{O}{||}}{C}-R'$ (Ketone) $+ H_2$

Example:1

1 – pentanol $\dfrac{Cu}{300^0C}$

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[300^0C]{Cu} CH_3CH_2CH_2CH_2-\overset{\overset{\large O}{||}}{C}-H + H_2$$

pentanal

Example:2

2 – pentanol $\dfrac{Cu}{300^0C}$

$$CH_3-\underset{\underset{\large OH}{|}}{CH}-(CH_2)_2-CH_3 \xrightarrow[300^oC]{Cu} CH_3-\underset{\underset{\large O}{||}}{C}-(CH_2)_2-CH_3 + H_2$$

2- pentanone

iii- Oxidation by oxidants

In case of excess alcohol (primary)

1^0 Alcohol: $RCH_2OH + Cr_2O_7^{2-} \rightarrow RCHO + Cr^{3+}$

Balanced equation:

$$3RCH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCHO + 2Cr^{3+} + 7H_2O$$

In case of excess oxidant:

$RCH_2OH + Cr_2O_7^{2-}$ (excess) $\rightarrow RCOOH + Cr^{3+}$

Balanced equation:

$$3RCH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3RCOOH + 4Cr^{3+} + 11H_2O$$

2^0Alcohol: $R-\underset{\underset{\large OH}{|}}{CH}-R' + Cr_2O_7^{2-} \rightarrow R-\overset{\overset{\large O}{||}}{C}-R' + Cr^{3+}$

Balanced equation:

$$3\ R-\underset{\underset{\large OH}{|}}{CH}-R' + Cr_2O_7^{2-} + 8H^+ \rightarrow 3\ R-\overset{\overset{\large O}{||}}{C}-R' + 2Cr^{3+} + 7H_2O$$

Example:1

Balance the following equation

$CH_3OH + Cr_2O_7^{2-} \rightarrow CH_2O + Cr^{3+}$(Acidic)

$$*(CH_3OH \rightarrow CH_2O + 2H^+ + 2e^-) \times 3$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$\left.\begin{array}{l} *3CH_3OH \rightarrow 3CH_2O + 6H^+ + 6e^- \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \end{array}\right\} \Rightarrow$$

$$\boxed{3CH_3OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_2O + 2Cr^{3+} + 7H_2O}$$

B) Esterification reaction

$$\text{Alcohol + carboxylic acid} \underset{\Delta}{\overset{H_2SO_4}{\rightleftarrows}} \text{Ester} + H_2O$$

$$ROH + R'-\overset{\overset{\large O}{||}}{C}-OH \underset{\Delta}{\overset{H_2SO_4}{\rightleftarrows}} R'-\overset{\overset{\large O}{||}}{C}-OR + H_2O$$

Example:1

1 – propanol + ethanoic acid ⇄ propyl ethanoate

$$CH_3-CH_2-CH_2OH + CH_3COOH \rightleftarrows CH_3COOCH_2CH_2CH_3 + H_2O$$

Example:2

1-pentanol + pentanoic acid $\rightleftarrows$

$$CH_3CH_2CH_2CH_2COOH + CH_3CH_2CH_2CH_2CH_2OH \underset{\Delta}{\overset{H_2SO_4}{\rightleftarrows}}$$

$$CH_3CH_2CH_2CH_2-\overset{\overset{\large O}{||}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_3 + H_2O$$

- **Important notes on esterification reaction:**
  - **Characteristics of an esterification reaction:**

    ⁎ Slow ⁎Reversible ⁎Athermic
  - H_2SO_4 has a kinetic role it increases the rate of the reaction.
  - H_2SO_4 is a dehydrating agent using it in large quantity makes the reaction shifted in the forward sense increasing the yield of the esterfication reaction.
  - Using a mixture of reactants which isn't equimolar makes the reaction shifted in the forward sense increasing the yield of esterfication reaction.

- Heating increases the rate of esterification reaction, but it doesn'taffect the yield since the reaction is athermic.

- **Alcohol +carboxylic acid ⇄Ester + H_2O**

t = 0 n_0 n'_0 0 0

t = t $n_0 - x$ $n'_0 - x$ x x

- $$\% \text{ yield} = \frac{\text{act.quantity}}{\text{theo quantity}} \times 100$$

Actual quantity = x

(Theoretical quantity found by st.ratio (Assume that the reaction is complete)

- $$K_c = \frac{[\text{Ester}][H_2O]}{[\text{Alcohol}][\text{Acid}]} = \frac{\frac{x}{V}\frac{x}{V}}{\frac{n_0 - x}{V}\frac{n'_0 - x}{V}} = \frac{x^2}{(n_0 - x)(n'_0 - x)}$$

- $$\alpha \text{ (alcohol)} = \frac{\text{n diss}}{\text{n initial}} = \frac{x}{n_0}$$

- **Industrial reactions:**

Formation of ethanol from ethene: $CH_2=CH_2 + H_2O \rightarrow CH_3 - CH_2OH$

Fermentation of glucose: $C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2C_2H_5OH + 2CO_2$

Formation of methanol: $CO + 2H_2 \rightarrow CH_3OH$

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Note:

Naming of aldehyde:

H – CHO	**methanal**
CH_3 – CHO	**ethanal**
CH_3 – CH_2 – CHO	**propanal**
CH_3 – CH_2 – CH_2 – CHO	**butanal**

$$\begin{array}{ccccccccc} & & & & & & \overset{\displaystyle O}{\|} & & \\ CH_3 & – & CH_2 & – & CH & – & CH & – & C – H \\ & & & & | & & | & & \\ & & & & CH_3 & & CH_3 & & \end{array}$$

2,3-dimethyl pentanal

Naming of ketones:

CH_3 – CO – CH_3 **propanone**

CH_3 – CH_2 – CO – CH_3 **2-butanone**

CH_3 – CH_2 – CH_2 – CO – CH_3 **2- pentanone**

CH_3 – CH_2 – CO – CH_2 – CH_3 **3- pentanone**

$$\begin{array}{ccccccccc} & & CH_3 & & & & & & O \\ & & | & & & & & & \| \\ CH_3 & – & CH & – & CH_2 & – & CH & – & C – CH_3 \\ & & & & & & | & & \\ & & & & & & CH_3 & & \end{array}$$

3,5-dimethyl-2-hexanone

Naming of carboxylic acid:

H – COOH	**methanoic acid**
CH_3 – COOH	**ethanoic acid**
CH_3 – CH_2 – COOH	**propanoic acid**
CH_3 – CH_2 – CH_2 – COOH	**butanoic acid**

Naming of ester:

$$\begin{array}{c} \qquad\quad O \\ \qquad\quad \| \\ CH_3CH_2 – C – OCH_3 \end{array}$$

methyl propanoate

$$\begin{array}{c} \qquad\quad O \\ \qquad\quad \| \\ CH_3CH_2CH_2 – C – O – CH_2CH_2CH_3 \end{array}$$

propyl butanoate

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Problems

Exercise: 1

Give the systematic (IUPAC) name and the class of each of the following alcohols

4) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$

5) $$(CH_3)_2 - CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2\ OH$$

6) $$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_2 - CH_3$$

7) $$(CH_3)_2 - CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - (CH_2)_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

8) $$(CH_3)_2 - CH - \underset{\displaystyle C_2H_5}{\underset{|}{CH}} - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

9) $$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \underset{\displaystyle C_2H_5}{\underset{|}{CH}} - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_2 - CH_3$$

Solution

1) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$: **1 – pentanol (primary)**

2)
$$\begin{array}{ccccccccccc} CH_3 & - & CH & - & CH & - & CH & - & CH_2 & - & OH \\ & & | & & | & & | & & & & \\ & & CH_3 & & CH_3 & & CH_3 & & & & \end{array}$$
2,3,4 - trimethyl - 1 -pentanol (primary)

3)
$$\begin{array}{ccccccccccc} & & & & & & CH_3 & & & & \\ & & & & & & | & & & & \\ CH_3 & - & CH & - & CH & - & CH & - & CH_2 & - & CH_3 \\ & & | & & | & & & & & & \\ & & OH & & CH_3 & & & & & & \end{array}$$
3,4- dimethyl- 2 -hexanol (secondary)

4)
$$\begin{array}{ccccccccccccc} CH_3 & - & CH & - & CH & - & CH_2 & - & CH_2 & - & CH & - & CH_3 \\ & & | & & | & & & & & & | & & \\ & & CH_3 & & CH_3 & & & & & & OH & & \end{array}$$
5,6- dimethyl- 2-heptanol (secondary)

5)
$$\begin{array}{ccccccccc} CH_3 & - & CH & - & CH & - & CH & - & CH_3 \\ & & | & & | & & | & & \\ & & CH_3 & & C_2H_5 & & OH & & \end{array}$$
3- ethyl- 4 –methyl- 2-pentanol (secondary)

6)
$$\begin{array}{ccccccccccc} & & & & & & CH_3 & & & & \\ & & & & & & | & & & & \\ CH_3 & - & CH & - & CH & - & C & - & CH_2 & - & CH_3 \\ & & | & & | & & | & & & & \\ & & CH_3 & & C_2H_5 & & OH & & & & \end{array}$$
4- ethyl- 3, 5- dimethyl -3-hexanol (tertiary)

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Exercise: 2

Write the equation of each of the following reactions using condensed structural formula. Name the organic compounds obtained

1) 1 – propanol + ethanoic Acid $\rightleftarrows$

2) 1 – pentanol $\xrightarrow[300^0C]{Cu}$

3) 2 – pentanol $\xrightarrow[(300^0C)]{Cu}$

4) 1- butanol + ½ O_2 $\xrightarrow[\Delta]{Cu}$

5) 2- butanol + ½ O_2 $\xrightarrow[\Delta]{Cu}$

6) 2- methyl -1- propanol + O_2 $\xrightarrow[\Delta]{Cu}$

Solution

1) 1 – propanol + ethanoic acid $\rightleftarrows$ propyl ethanoate

$$CH_3 - CH_2 - CH_2OH + CH_3COOH \rightleftarrows CH_3COOCH_2CH_2CH_3 + H_2O$$

2) 1 – pentanol $\xrightarrow[300^0C]{Cu}$

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[300^0C]{Cu} CH_3CH_2CH_2CH_2 - \underset{}{\overset{\overset{\displaystyle O}{||}}{C}} - H + H_2$$

pentanal

3) 2 – pentanol $\xrightarrow[(300^0C)]{Cu}$

$$\underset{\underset{\displaystyle OH}{|}}{CH_3 - CH} - (CH_2)_2 - CH_3 \xrightarrow[300^oC]{Cu} CH_3 - \underset{\underset{\displaystyle O}{||}}{C} - (CH_2)_2 - CH_3 + H_2$$

2- pentanone

4) 1- butanol + ½ O_2 $\xrightarrow[\Delta]{Cu}$

$$CH_3CH_2CH_2CH_2OH + ½\ O_2 \xrightarrow[\Delta]{Cu} CH_3CH_2CH_2 - \overset{\overset{\displaystyle O}{||}}{C} - H + H_2O$$

butanal

5) 2- butanol + ½ O_2 $\xrightarrow[\Delta]{Cu}$

$$\underset{\displaystyle OH}{CH_3-\underset{|}{CH}}-CH_2-CH_3 + \tfrac{1}{2}O_2 \xrightarrow[\Delta]{Cu} CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_3 + H_2O$$

butanone

6) 2- methyl -1- propanol + O_2 $\xrightarrow[\Delta]{Cu}$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH + O_2 \xrightarrow[\Delta]{Cu} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-OH + H_2O$$

2- methyl propanoic acid

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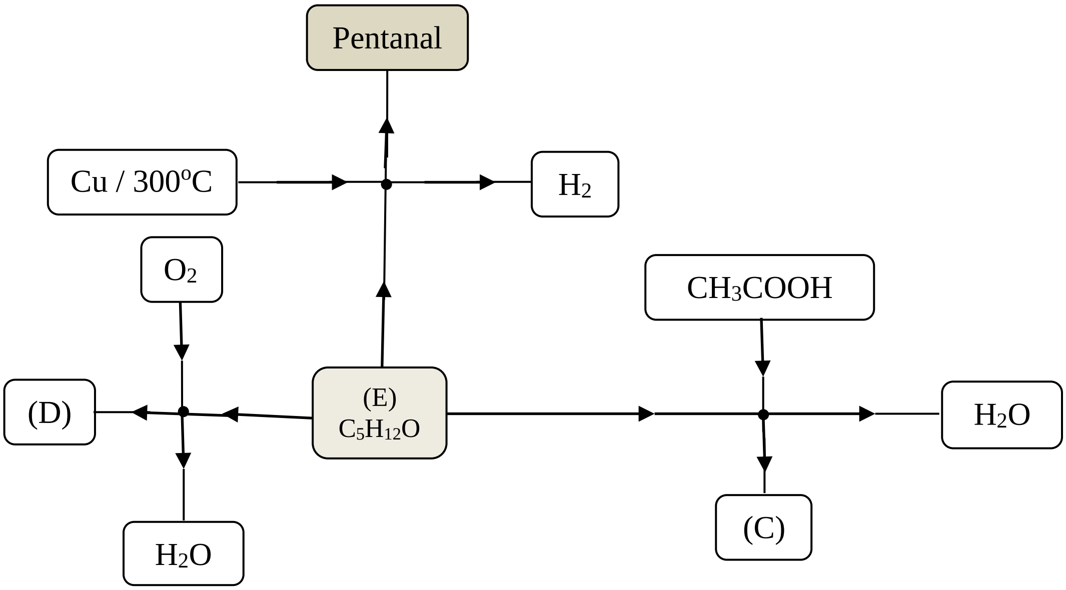
Exercise: 3

Identify the compounds (C), (D) and (E) in the map below (C.S.F and name).



Solution

(E) $\xrightarrow[300°C]{Cu}$ pentanal

Since upon catalytic dehydrogenation of (E) an aldehyde is formed, (E) is a primary alcohol.

c.s.f of pentanal: $CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-H$

so (E) is 1- pentanol, its c.s.f: $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

(E) + O_2 $\xrightarrow[\Delta]{Cu}$ (D)

$$CH_3-CH_2-CH_2-CH_2-CH_2-OH + O_2 \xrightarrow[\Delta]{Cu} CH_3-CH_2-CH_2-CH_2-COOH + H_2O$$

so (D) is pentanoic acid

(E) + $CH_3COOH \rightarrow$ (C) + H_2O

$$CH_3COOH + CH_3-CH_2-CH_2-CH_2-CH_2-OH \rightleftarrows$$

$$CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_3 + H_2O$$

(C): pentyl ethanoate

Exercise: 4

How could you prepare? (using condensed structural formula).

1) Propanone starting from 2–propanol.

2) 2–butyl ethanoate starting from ethanoic acid.

3) 2–methyl propanoic acid ($CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$) starting from 2–methyl–1–propanol

4) ethanol starting from glucose.

5) ethanoic acid starting from ethene (3 steps).

Solution

1) $$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[300^oC]{Cu} \underset{\text{(propanone)}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3} + H_2$$

2) $$CH_3COOH + CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \rightleftarrows CH_3-\overset{\overset{O}{||}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 + H_2O$$

3) $$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + 1/2\ O_2 \xrightarrow[\Delta]{Cu} CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH + H_2O$$

4) $$C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + 2CO_2$$

5) $$CH_2=CH_2 + H_2O \rightarrow CH_3-CH_2OH$$

$$CH_3-CH_2OH + ½\ O_2 \xrightarrow{Cu/\Delta} CH_3-CHO + H_2O$$

$$CH_3-CHO + ½\ O_2 \xrightarrow{Cu/\Delta} CH_3-COOH$$

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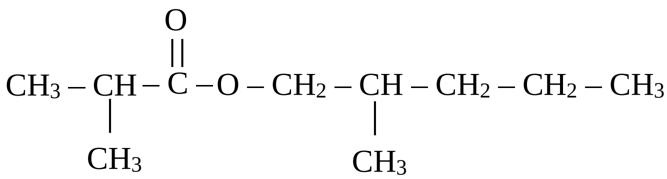
Exercise: 5

Consider three alcohols (A),(B) and (F).

(A): 2–methyl–1–pentanol **(B): 2–methyl–3–pentanol**

(F): 1–hexanol

1) Precise the type of isomerism between (A) and (B) and between (A)and (F).
2) Write the condensed structural formula of (A), (B) and (F).
3) **(A) reacts with an acid (L) to give a compound (D) whose condensed structural formula:**



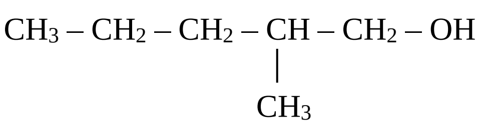
   a) Recopy the condensed structural formula of compound (D), circle and name its functional group.
   b) Write the condensed structural formula of the acid (L). Give its name.

Solution

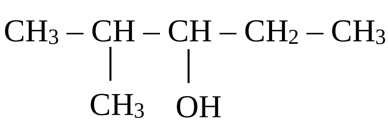
1) • (A) and (B) are positional isomers

• (A) and (F) are skeletal isomers

2) (A):

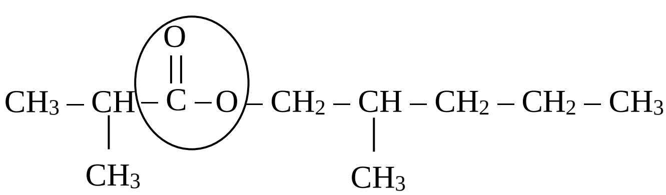


(B):



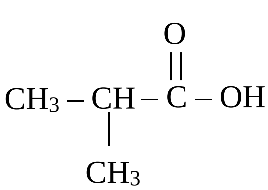
(F): $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - OH$

3) a)



Functional group: ester group (– COO–)

b) Acid (L):



Name: 2- methyl propanoic acid

Exercise: 6

Catalytic reactions of Alcohols

A saturated mono alcohol (A): C_xH_yO has the following mass percent composition:

% H = 13.51 %   % O = 21.62 %

A) Molecular formula and Isomerism

1) Show that the molecular formula of (A) is $C_4H_{10}O$.
2) Write the condensed structural formula of all possible isomers of compound (A). Name each one.

B) Dehydrogenation Reaction:

The two unbranched isomers undergo dehydrogenation reaction at a temperature of 300°C and in absence of oxygen using Cu as a catalyst.

1) Write using condensed structural formulas the equations of the reactions that took place.
2) Indicate the family and the name of the organic compounds obtained.
3) The above reactions show the mild oxidation of an alcohol. Define mild oxidation.

C) Esterfication reaction

A mixture of 0.2 mol of ethanoic acid and a volume V = 20mL of the unbranched primary isomer of alcohol (A) is heated in presence of few drops of concentrated sulfuric acid until having a constant quantity of ester. This quantity is 0.13mol.

1) Write the equation of this reaction. Name the obtained organic compound.
2) Verify that the initial reactants are in equimolar amounts.
3) Calculate the equilibrium constant K_c of the esterfication reaction.
4) Determine the % yield of the esterfication reaction.

Given: $\rho_{(alcohol)}$:0.74 g/mL   C = 12   H = 1   O = 16 g/mol

Solution

A) (A): C_xH_yO

1) % H = 13.51 %   % O = 21.62 %

% C = 100 – (% H + % O) = 100 – (21.62 + 13.51) = 64.87 %

Apply law of proportionality:

$$\frac{12\,x}{\%\,C} = \frac{Y}{\%\,H} = \frac{16\,z}{\%\,O} \qquad z = 1$$

$$\frac{12\,x}{64.87} = \frac{Y}{13.51} = \frac{16\,(1)}{21.62};$$

x = 4, y = 10

Molecular formula of (A): $C_4H_{10}O$

2) Isomers of (A)

$CH_3 - CH_2 - CH_2 - CH_2 - OH$ 1 – butanol

$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3$ 2 – butanol

$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - OH$ 2 – methyl – 1 – propanol

$CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$ 2 – methyl – 2 – propanol

B) 1) $CH_3CH_2CH_2CH_2OH \xrightarrow[300^oC]{Cu} CH_3CH_2CH_2 - \overset{\overset{O}{||}}{C} - H + H_2$ **equation (1)**

$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3 \xrightarrow[300^oC]{Cu} CH_3 - \overset{\overset{O}{||}}{C} - CH_2 - CH_3 + H_2$ **equation (2)**

2) butanal Its family is: aldehyde
butanone Its family is: ketone

3) It is a reaction where there is no breakage in the carbon chain. (number of carbon atoms is conserved).

C) 1) Ethanoic acid + 1- butanol $\begin{cases} V = 20 \text{ ml} \\ ʃ = 0.74 \text{ g/mL} \end{cases}$

n = 0.2 mol

$CH_3 - \overset{\overset{O}{||}}{C} - OH + CH_3CH_2CH_2CH_2OH \rightleftarrows$

$CH_3 - \overset{\overset{O}{||}}{C} - O - CH_2 - CH_2 - CH_2 - CH_3$ (1-butyl ethanoate) $+ H_2O$

2) ʃ alcohol = $\frac{m}{V}$; m = ʃ × V = 0.74 g/mL × 20 mL = 14.8 g

n (alcohol) = $\frac{m}{M} = \frac{14.8}{74}$ = 0.2 mol, since n(alc)=n(acid) = 0.2 mol ⇒ equimolar mixture

3)

	Acid	+	Alcohol	⇄	Ester	+	H_2O
t = 0	0.2 mol		0.2 mol		0		0
t: eq	0.2 – x		0.2 – x		xx		

$$K_C = \frac{[Ester][H_2O]}{[Acid][Alcohol]} = \frac{\frac{x}{V}.\frac{x}{V}}{\frac{0.2-x}{V}.\frac{0.2-x}{V}} = \frac{x^2}{(0.2-x)^2}$$

At equilibrium; n (ester) = x = 0.13 mol

$$K_C = \frac{(0.13)^2}{(0.2-0.13)^2} = 3.44$$

4) % yield = $\frac{\text{actual quantity}}{\text{theoretical quantity}} \times 100$

Actual quantity = x = 0.13 mol

We assume that the reaction is complete

n(ester theoretical) = n (Alcohol) = 0.2 mol

% yield = $\frac{0.13}{0.2} \times 100 = 65$ %

****

Exercise: 7 **From an Alcohol to Carbonyl compounds**

The complete combustion of 2.2g of an alcohol (A) of formula C_xH_yO gives 5.5g of carbon dioxide gas and 2.7g of water vapor.

A) <u>Molecular formula and Isomerism</u>

1) Show that the molecular formula of (A) is $C_5H_{12}O$.
2) Write all possible isomers of (A).

B) <u>Yield of a reaction</u>

0.2 mol of an isomer (B) of the above alcohol is treated with propanoic acid to give 19.29g of an ester (E) of formula:

$$\begin{array}{c} \overset{\displaystyle O}{\overset{\|}{C}} - O - CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3 \end{array}$$

$$CH_3 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O - CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3$$

1) Give the IUPAC name of the ester formed.
2) Deduce the condensed structural formula and the class of (B).
3) Write the equation of the reaction.
4) Determine the % yield of the reaction.

C) <u>Some reactions of the alcohol (B)</u>

In presence of Cu and in the absence of air, the isomer (B) is subjected to dehydrogenation at 300^0C to give an organic compound (C).

1) Write the equation of the reaction that took place.
2) Name compound (C). Give its class.
3) Verify if the above transformation is a mild oxidation reaction.

D) <u>Oxidation by an oxidant</u>

An isomer of alcohol (A) is heated with acidified potassium dichromate.A compound (D) is obtained whose condensed structural formula is shown below:

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_2 - CH_3$$

1) Give the IUPAC name of compound (D). Give its class.
2) Deduce the condensed structural formula of the isomer of (A).
3) Write using condensed structural formulathe oxidation and reduction half reactions. Deduce the overall reaction.

Given: C = 12 H = 1 O = 16 g/mol

Solution

A) 1) 2.2 g of $C_xH_yO + O_2 \rightarrow$ 5.5 g CO_2 and 2.7 g H_2O

*$C + O_2 \rightarrow CO_2$

$n(CO_2) = \frac{m}{M} = \frac{5.5}{44} = 0.125$ mol ; $\quad \frac{n\,(C)}{1} = \frac{n\,(CO_2)}{1} = 0.125$ mol

$n(C) = \frac{m}{M} \rightarrow m = n \times M = 0.125 \times 12 = 1.5$ g

$\%\,C = \frac{m\,(C)}{m\,(cpd)} \times 100 = \frac{1.5}{2.2} \times 100 = 68.18\,\%$

*$H_2 + ½\,O_2 \rightarrow H_2O$

$n(H_2O) = \frac{m}{M} = \frac{2.7}{18} = 0.15$ mol ; $\quad \frac{n\,(H_2)}{1} = \frac{n\,(H_2O)}{1}$; $n(H_2) = 0.15$ mol

$n(H_2) = \frac{m}{M} \rightarrow m = n \times M = 0.15 \times 2 = 0.3$ g

$\%\,H = \frac{m\,(H)}{m\,(cpd)} \times 100 = \frac{0.3}{2.2} \times 100 = 13.63\,\%$

$\%\,O = 100 - (68.18 + 13.63) \longrightarrow \%\,O = 18.19\,\%$

Apply law of proportionality

$$\frac{12\,x}{\%\,C} = \frac{Y}{\%\,H} = \frac{16\,z}{\%\,O} \longrightarrow \frac{12\,x}{68.18} = \frac{Y}{13.63} = \frac{16\,(1)}{18.19}$$

$x = 5$, $y = 12 \Rightarrow$ Molecular formula of (A): $C_5H_{12}O$

2) Isomers of $C_5H_{12}O$

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$ 1-pentanol

$$\begin{array}{c} CH_3 - CH_2 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 \end{array}$$

2-pentanol

$$\begin{array}{c} CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3 \end{array}$$

3-pentanol

2-methyl-1-butanol

$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - OH$$

3-methyl-1-butanol

$$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_2 - OH$$

2-methyl-2-butanol

$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

3-methyl-2-butanol

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

2,2-dimethyl-1-propanol

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-OH$$

B) 0.2 mol of (B) + propanoic acid → (E)

1) (E): 2- methyl butyl propanoate

2) (B): 2- methyl-1-butanol

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$$

the alcohol (B) is a primary alcohol

3) $$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-OH + CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH \rightleftharpoons$$

$$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3 + H_2O$$

4) $m_{(actual)} = 19.29g$

Using st.ratio: $\frac{n\text{ (Alcohol)}}{1} = \frac{n\text{ (ester)}}{1}$

n(ester) = 0.2 mol M(ester) = 144 g/mol

$n = \frac{m}{M} \rightarrow m = n \times M = 0.2 \times 144 = 28.8$ g

% yield = $\frac{\text{act mass}}{\text{theo mass}} \times 100 = \frac{19.29}{28.8} \times 100 = 67$ %

C)

1) $$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH \xrightarrow[300^0]{Cu} CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-H + H_2$$

2) (C): 2 – methyl butanal, it is an aldehyde.

3) The above transformation is a mild oxidation reaction since there is no breakage in the carbon chain.

D) $$(A) + Cr_2O_7^{2-} \rightarrow CH_3-\overset{\overset{O}{||}}{C}-(CH_2)_2-CH_3 \quad + Cr^{3+}$$

1) (D) is a ketone, it is called 2-pentanone.

2) Since (D) is a ketone then (A) must be a secondary alcohol,

it is 2-pentanol (A): $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3$

3) $$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3 + Cr_2O_7^{2-} \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-(CH_2)_2-CH_3 + Cr^{3+}$$

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3 \rightarrow CH_3-\overset{\overset{O}{||}}{C}-(CH_2)_2-CH_3 + 2H^+ + 2e^-$$

(Multiply by 3)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

<u>Over all reaction:</u>

$$3\,CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3 + Cr_2O_7^{2-} + 8H^+ \rightarrow 3\,CH_3-\overset{\overset{O}{||}}{C}-(CH_2)_2-CH_3 + 2Cr^{3+} + 7H_2O$$

****

Exercise: 8 **Identification of an Alcohol and Some reactions of Alcohols**

The oxidation of a 0.55 g of a non-branched primary alcohol (A) gives an acid (B) which is titrated with an aqueous sodium hydroxide solution of concentration C = 0.5 mol/L.The equivalent point is reached when12.5 mL of the basic solution is added.

A) <u>Identification of organic compounds (A) and (B)</u>

1) Determine the molecular formula of compound (A).
2) Write the condensed structural formula of compounds (A) and (B). Name each one of them.

B) <u>Some catalytic reactions of the alcohol (A)</u>

The dehydrogenation of alcohol (A) takes place at a temperature of 300°C and in absence of oxygen using Cu as a catalyst to give compound (C). Moreover, alcohol (A) undergoes a dehydration reaction in the presence of Al_2O_3 as a catalyst, an alkene is obtained as one of the products.

1) Write the equation of the dehydrogenation reaction using condensed structural formula.
2) Indicate the family and the name of the organic compound (C) obtained.
3) Draw a conclusion about the choice of catalysis in the dehydrogenation reaction and in the dehydration reaction of alcohol (A).

C) <u>Esterfication reaction</u>

An equimolar mixture of 1 mol of the two compounds (A) and (B) react in presence of few drops of sulfuric acid until equilibrium is attained.

1) Write the equation of the esterfication reaction. Give its characteristics.
2) Name the ester (E) formed.
3) Indicate the role of sulfuric acid used in the above reaction.
4) Calculate the % yield of the esterification reaction if the equilibrium constant of the above reaction is $K_c = 4.12$.
5) Suggest two methods to increase the yield of the above reaction.

Given: C = 12 H = 1 O = 16 g/mol

Solution

A) 0.55 g of a non-branched primary alcohol (A) + $O_2 \longrightarrow$ carboxylic acid (B)

$$(B) \neq NaOH \begin{cases} C_B = 0.5 \text{ mol/L} \\ V_{BE} = 12.5 \text{ mL} \end{cases}$$

1) $RCOOH + OH^- \rightarrow RCOO^- + H_2O$

At eq point: n (RCOOH) = n (OH^-)

n (RCOOH) = $C_B \times V_{BE} = 0.5 \times 12.5 \times 10^{-3}$ mol

n (B) = n (RCOOH) = 6.25×10^{-3} mol

Using st.ratio:

n (A) = n (B) $\longrightarrow$ n (Alcohol) = 6.25×10^{-3} mol

n (Alcohol) = $\frac{m}{M}$; $\quad M = \frac{m}{n} = \frac{0.55}{6.25 \times 10^{-3}} = 88$ g/mol

M ($C_nH_{2n+2}O$) = 88

$12n + 2n + 2 + 16 = 88 \longrightarrow 14n + 18 = 88 \longrightarrow 14n = 70 \longrightarrow n = \frac{70}{14} = 5$

Molecular formula of (A): $C_5H_{12}O$

2) (A) $C_5H_{12}O$: $CH_3CH_2CH_2CH_2CH_2OH$: 1 – pentanol

(B): $CH_3CH_2CH_2CH_2-\overset{\overset{\large O}{||}}{C}-OH$:pentanoic acid

B) 1)

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[300^0C]{Cu} \underset{\text{pentanal}}{CH_3CH_2CH_2CH_2}-\overset{\overset{\large O}{||}}{C}-H + H_2$$

2) The organic compound (C) produced is pentanal

It belongs to aldehyde family.

3) 1-pentanol $\xrightarrow[300^oC]{Cu}$ pentanal + H_2

1-pentanol $\xrightarrow{Al_2O_3}$ alkene + H_2O

The above reaction shows the selectivity of a catalyst (A catalyst directs a chemical reaction).

C) 1) $CH_3CH_2CH_2CH_2COOH + CH_3CH_2CH_2CH_2CH_2OH \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}}$

$$CH_3CH_2CH_2CH_2-\overset{\overset{\large O}{||}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_3 + H_2O$$

Characteristics: slow, reversible and athermic.

2) (E): pentyl pentanoate

3) H_2SO_4 has a kinetic role, it increases the rate of esterification reaction

4) Acid + Alcohol ⇄ Ester + H_2O

	Acid	Alcohol	Ester	H_2O
t = 0	1 mol	1 mol	0	0
t = teq	1 – x	1 – x	x	x

$$K_C = \frac{[\text{Ester}][H_2O]}{[\text{Acid}][\text{Alcohol}]} = \frac{\frac{x}{V}\cdot\frac{x}{V}}{\frac{1-x}{V}\cdot\frac{1-x}{V}} = \frac{x^2}{(1-x)^2} = \frac{x^2}{(1-x)^2}$$

$4.12 = \frac{x^2}{(1-x)^2} \rightarrow x = 0.67$

% yield = $\frac{\text{act quantity}}{\text{theo quantity}} \times 100$ Actual quantity = x = 0.67

Assume that reaction is complete, n theoretical = n alcohol = 1mol

% yield = $\frac{0.67}{1} \times 100 = 67\ \%$

5) To increase the yield of esterification reaction

- We may use a mixture of reactants which isn't equimolar thus the reaction is shifted in the forward sense increasing the yield of esterification reaction.
- We use H_2SO_4 in a large amount, H_2SO_4 is a dehydrating agent it eliminates water this makes the reaction shifted in the direction of formation of ester thus the yield of esterification reaction increases.

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Exercise: 9 **Organic compounds**

Given the following set of compounds:

(A): $CH_3 - CH_2 - CH_2 - CH_2 - OH$ (B): $CH_3CH_2 - CH_2 - CHO$

(C): $CH_3 - CH_2 - \overset{\overset{\displaystyle O}{||}}{C} - CH_3$

(D): $CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - OH$

(E): $CH_3 - CH_2 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_3$

(F): $CH_3 - CH_2 - CH_2 - COOH$

A) **<u>Isomers and functional groups</u>**

1) Give the systematic name of each of the above compounds and circle the corresponding functional groups.
2) Specify the isomerism type of each set of the two compounds(A, E), (B, C) and (E, D).

B) **<u>Organic reactions on different compounds</u>**

1) Write the equation of the reaction to prepare (B) starting from (A).
2) Write the equation of the reaction to prepare (C) starting from (E).
3) Write the equation of the reaction to prepare (F) starting from (A).

C) **<u>Oxidation of alcohols by potassium permanganate.</u>**

10 mL of each of the alcohols (A), (D) and (E) are poured in three tubes then treated with excess potassium permanganate solution $KMnO_4$.The obtained results are given in the table below:

Tubes	**Results of the reaction with $KMnO_4$**
1	Formation of compound (F)
2	Formation of compound (C)
3	Negative result

1) Analyze the results in the above table.
2) Identify the content of each tube.

D) **<u>Synthesis reaction</u>**

A volume V_1 = 20 mL of (A) and volume V_2 of (F) are introduced into a round bottom flask, 2 mL of sulfuric acid is added into the flask. The mixture is heated for about 20 min.An ester of mass 25g is obtained.

1) Write the equation of the esterification reaction.
2) Indicate the purpose of heating.

3) Determine the volume V_2 of (F) so that the reactants are in stochiometric proportion.
4) Calculate the yield of the esterification reaction.

Given: ʃ(A) = 0.81 g/ml   ʃ(F) = 0.95 g/ml

C = 12   H = 1   O = 16   g/mol

Solution

A)

1) (A) : $CH_3 - CH_2 - CH_2 - CH_2\boxed{OH}$ 1- butanol

(B): $CH_3CH_2CH_2\boxed{CHO}$ butanal

(C): $CH_3CH_2 - \boxed{\overset{O}{\overset{||}{C}}} - CH_3$ 2-butanone

(D): $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \boxed{OH}$ 2-methyl-2-propanol

(E): $CH_3 - CH_2 - \underset{\boxed{OH}}{CH} - CH_3$ 2-butanol

(F): (F): $CH_3CH_2CH_2\boxed{COOH}$ butanoic acid

2) (A) and (E) are positional isomers, (B) and (C) are functional isomers, (E) and (D) are skeletal isomers.

B)

1) $CH_3CH_2CH_2CH_2OH \xrightarrow[300^0C]{Cu} CH_3CH_2CH_2 - \overset{O}{\overset{||}{C}} - H + H_2$

2) $CH_3 - CH_2 - \underset{OH}{CH} - CH_3 + \frac{1}{2} O_2 \xrightarrow[\Delta]{Cu} CH_3CH_2 - \overset{O}{\overset{||}{C}} - CH_3 + H_2O$

3) $CH_3CH_2CH_2CH_2OH + O_2 \xrightarrow[\Delta]{Cu} CH_3 - CH_2 - CH_2 - \overset{O}{\overset{||}{C}} - OH + H_2O$

C)

1) In tube (1): the addition of excess oxidant gives a carboxylic acid (F) thus in tube (1) there is a primary alcohol.

In tube (2): the addition of excess oxidant gives ketone (C) thus in tube (2) there is a secondary alcohol.

In tube (3): the addition of excess oxidant gives a negative result thus in tube (3) there is a tertiary alcohol.

2) Tube (1) contains compound (A): 1-butanol

Tube (2) contains compound (E): 2 -butanol

Tube (3) contain compound (D): 2-methyl-2-propanol

D)

1) $CH_3(CH_2)_3OH + CH_3(CH_2)_2COOH \rightleftarrows CH_3\text{-}(CH_2)_2COO\,(CH_2)_3\text{-}CH_3 + H_2O$

2) Heating increases the rate of esterification reaction.

3) n (Alcohol) = n (acid)

$$\frac{m}{M} = \frac{m}{M} \longrightarrow \frac{(\int\times V)\text{alcohol}}{\text{M (alcohol)}} = \frac{(\int\times V)\text{Acid}}{\text{M acid}} \longrightarrow \frac{0.81\times20}{74} = \frac{0.95\times V_2}{88} \longrightarrow V_2 \text{ acid} = 20.27 \text{ ml}$$

4) $\frac{\text{n (alcohol)}}{1} = \frac{\text{n Ester}}{1} \longrightarrow \frac{\int\times V}{M} = n(\text{Ester}) \longrightarrow n(\text{Ester}) = \frac{0.81\times20}{74} = 0.219 \text{ mol}$

$n(\text{Ester}) = \frac{m}{M} \longrightarrow m(\text{Ester}) = n \times M = 0.219 \times 144 = 31.536 \text{ g}$

$\%\text{ yield} = \frac{\text{actual mass}}{\text{theoretcal mass}} \times 100 = \frac{25}{31.536} \times 100 = 79.27\%$

****

Exercise: 10

Esterification Reaction

For an equimolar amount of a mono alcohol and a mono carboxylic acid the % yield of the reaction at equilibrium is as follows:

Class of alcohol	Primary alcohol	Secondary alcohol	Tertiary alcohol
% yield	67 %	60 %	5 %

42.85 ml of an alcohol (A) is introduced into a round bottom flask with propanoic acid (B) to give an ester (E): $C_nH_{2n}O_2$ of molar mass 116 g/mol as shown in the reaction:

$$\textbf{(A) + (B)} \rightleftharpoons \textbf{(E)} + H_2O$$

Given: The initial mixture in equimolar amounts.

A) <u>Molecular formula of (E) and (A):</u>

1) Determine the molecular formula of ester (E).
2) Show that the molecular formula of (A) is C_3H_8O.

B) <u>Study of the results of the esterification reaction:</u>

1) Determine the number of moles of each of alcohol (A) and the acid (B) initially introduced if $\int_{(A)} = 0.84$ g/ml.

   The acid left in the flask is titrated and the results are recorded in the following table:

t (sec)	0	10	20	30	40	80	130	150
n acid (mol)	0.6	0.48	0.39	0.33	0.28	0.22	0.2	0.2

2) Plot the curve n (acid) = f (t)

   Take the scale: 1 cm $\rightarrow$ 0.1 mol   1 cm $\rightarrow$ 20 sec
3) Determine the composition of the mixture at equilibrium.
4) Determine the % yield of the reaction.
5) Identify the alcohol (A).
6) Write the equation of the esterification reaction. Name the ester obtained.

C) <u>Catalytic reactions of alcohol (A):</u>

The primary isomer of alcohol (A) undergoes catalytic oxidation in presence of oxygen and Cu as a catalyst to give two organic compounds:

$$\mathbf{A} + \frac{1}{2}O_2 \rightarrow \mathbf{(B)} + \ldots\ldots \qquad\qquad \mathbf{A} + O_2 \rightarrow \mathbf{(C)} + \ldots\ldots$$

1) Copy and complete the above reactions using condensed structural formula.
2) Name the organic compounds (B) and (C) obtained.

Solution

42.85ml of (A) + (B) $\rightarrow$ (E) + H_2O

A) 1) M (E) = 116 g/mol

M ($C_nH_{2n}O_2$) = 116

$12n + 2n + 32 = 116 \Rightarrow 4n = 84 \Rightarrow n = 6 \Rightarrow$ M.F of (E): $C_6H_{12}O_2$

2) Let (A) be $C_xH_yO_z$ M.F (propanoic acid): $C_3H_6O_2$

$C_xH_yO_z + C_3H_6O_2 \rightarrow C_6H_{12}O_2 + H_2O$

According to the law of conservation of atoms:

The total number of atom in the reactants = Total number of atoms in the products

<u>w.r.t (C)</u>: $x + 3 = 6 \Rightarrow x = 3$ **<u>w.r.t (H)</u>:** $y + 6 = 12 + 2 \Rightarrow y = 8$

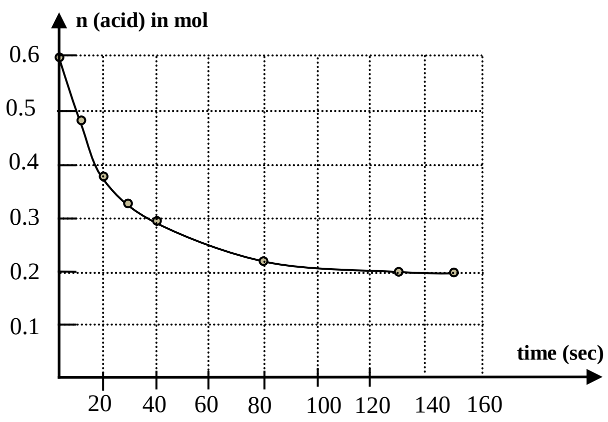
<u>w.r.t (O)</u>: $z + 2 = 2 + 1 \Rightarrow z = 1$

M.F of (A): C_3H_8O

B) 1) $n\,(A) = \dfrac{m}{M} = \dfrac{\int \times V}{M} = \dfrac{0.84\ g/ml \times 42.85\ ml}{60} = 0.6\ mol$

The initial mixture is in equimolar amounts: n (acid) = n (alcohol) = 0.6 mol

2)



3) Alcohol + acid $\rightarrow$ Ester + H_2O

	Alcohol	acid	Ester	H_2O
t =0	0.6 mol	0.6mol	0	0
$t = t_{eq}$	0.6 – x	0.6 – x	x	x

At equilibrium: n (acid) = 0.2 mol (from the table)

$0.6 - x = 0.2 \Rightarrow x = 0.4$ mol

At equilibrium: n (alcohol) = n (acid) = 0.2 mol

n (Ester) = n(H_2O) = 0.4 mol

4) $\% \text{ yield} = \dfrac{n\ act}{n\ th} \times 100 \Rightarrow n\ act = x = 0.4$ mol

Assume that the reaction is complete:

$\dfrac{n\ (\text{Ester th})}{1} = \dfrac{n\ (\text{acid})}{1} = 0.6$

$\% \text{ yield} = \dfrac{0.4}{0.6} \times 100 = 66.6\%$

5) The alcohol is primary alcohol since for an equimolar amount of primary alcohol and acid. The % yield is 67%, so C.S.f of (A) is: $CH_3 - CH_2 - CH_2OH$

Name: 1- propanol

6) $CH_3{-}CH_2{-}CH_2OH + CH_3{-}CH_2{-}\underset{}{\overset{\overset{\displaystyle O}{\|}}{C}}{-}OH \rightleftharpoons CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}CH_3 + H_2O$

Name of ester: propyl propanoate

C) 1) $CH_3\,CH_2CH_2\,OH + \frac{1}{2}\,O_2 \rightarrow CH_3\,CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + H_2O$ (B)

$CH_3\,CH_2CH_2\,OH + O_2 \rightarrow CH_3\,CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + H_2O$ (C)

2) (B): propanal (C): propanoic acid

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Exercise: 11 **Ethanol (an important industrial compound)**

In industry ethanol is produced by the fermentation of compound (A) according to the following reaction: $C_xH_yO_z \xrightarrow[\text{absence of air}]{\text{yeast}}$ **2ethanol + $2CO_2$**

A) <u>Production of ethanol by fermentation</u>

1) Give the molecular formula of ethanol; write its condensed structural formula.
2) Identify compound (A).
3) Indicate the role of yeast.
4) Justify why this fermentation is carried out in the absence of air.

B) <u>Esterification Reaction:</u>

A mixture of 0.5 mol of ethanol and 0.5 mol of ethanoic acid is heated, a reaction took place after a certain time it is found that the % yield of the reaction is 50%.

1) Write using condensed formula of the organic compounds the equation of this reaction.
2) Determine the composition of the mixture at the end of heating.
3) Verify if the equilibrium state is reached at the end of heating knowing that the equilibrium constant Kc is equal to 4.
4) The experiment described above is realized again by mixing 0.2 mol of ethanol and 0.2 mol of ethanoic acid under the same experimental conditions. Specify if the percentage yield of the reaction will change.

C) <u>Alcoholic degree of ethanol</u>

It is required to convert, using an enzyme 75L of ethanol solution of unknown alcoholic degree into vinegar. The volume of air needed is 2473.02L.

1) Write the equations of the enzymatic oxidation of ethanol.
2) Determine the alcoholic degree of the solution used.

Given: * $V_{air} = 5V_{O_2}$ $\int$(ethanol) = 0.8Kg/L V_m = 24 L/mol

* Alcoholic degree represents % volume composition of ethanol solution

*C = 12 O = 16 H = 1 g/mol

Solution

A) 1) Molecular formula of ethanol: C_2H_5OH

C.S.f: $CH_3 - CH_2 - OH$

2) $C_xH_yO_z \xrightarrow{\text{Yeast}} 2C_2H_6O + 2CO_2$

According to the law of conservation of atoms.

The number of atoms in the reactants = The number of atoms in the products

For C: $x = 2(2) + 2 \Rightarrow x = 6$

For H: $y = 2(6) \Rightarrow y = 12$

For O: $z = 2 + 2(2) \Rightarrow z = 6$

Molecular formula of (A): $C_6H_{12}O_6$

3) Yeast acts as a catalyst.

4) To prevent the mild oxidation of glucose.

B) 1) $CH_3\text{-}COOH + CH_3 - CH_2OH \rightleftarrows CH_3\text{-}COO - CH_2 - CH_3 + H_2O$

2)

	Acid	+	Alcohol	$\rightleftarrows$	Ester	+	H_2O
t = 0	0.5 mol		0.5 mol		0		0
t = t	0.5 – x		0.5 – x		xx		

% yield = $\frac{\text{act mole}}{\text{theo mole}} \times 100$

Assume that the reaction is complete

$$\frac{n(ester)}{1} = \frac{\text{n(acid)}}{1} = 0.5mol$$

$$50 = \frac{x}{0.5} \times 100 \text{ , x=} \frac{50 \times 0.5}{100} = 0.25mol$$

<u>At time = t</u>

n(ester) = n(H_2O) = 0.25 mol

n(acid) = n(alcohol) = 0.5 - 0.25 = 0.25mol

3) At time t,

$$Q = \frac{[\text{ester}] \times [H_2O]}{[\text{acid}] \times [alcohol]} = \frac{\frac{0.25}{V} \times \frac{0.25}{V}}{\frac{0.25}{V} \times \frac{0.25}{V}} \Rightarrow Q = 1$$

$Q \neq Kc$, the time tisn't the instant of equilibrium position.

4) Since the initial mixture of the acid and the alcohol remains in equimolar amounts, the actual amount and the theoretical amount decrease but the ratio remains constant

$\Rightarrow$ yield does not change.

C) ethanol $\{$ v = 75L + Vair = 2473.02L

1) $CH_3-CH_2-OH + \frac{1}{2} O_2 \xrightarrow{Cu/\Delta} CH_3-CHO + H_2O$

$CH_3-CHO + \frac{1}{2} O_2 \xrightarrow{Cu/\Delta} CH_3-COOH$ $\Big\} \Rightarrow$

$CH_3-CH_2-OH + O_2 \xrightarrow{Cu/\Delta} CH_3-COOH + H_2O$

2) $VO_2 = \frac{Vair}{5} = \frac{2473.02}{5} = 494.604L$

$nO_2 = \frac{V}{Vm} = \frac{494.604}{24} = 20.608mol$

Due to s.t ratio:

$\frac{nO_2}{1} = \frac{n\ ethanol}{1} \Rightarrow n\ ethanol = 20.608mol$ M(C_2H_5OH) = 46g/mol

m (ethanol) = n × M = 20.608 × 46 = 947.968g

$m = V \times \int \Rightarrow V = \frac{m}{\int} = \frac{947.968}{0.8 \times 1000} = 1.184L$

$\%\ by\ volume = \frac{V\ (ethanol)}{V\ (solution)} \times 100 = \frac{1.184}{75} \times 100 = 1.579\%$

$\Rightarrow$ alcoholic degree = 1.579°

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Exercise: 12 **Identification of an Alcohol by Esterification Reaction**

From an equimolar mixture of a mono alcohol and a mono carboxylic acid the % yield of reaction are as follows:

Class of alcohol	Primary alcohol	Secondary alcohol	Tertiary alcohol
% yield	67 %	60 %	5 %

The elemental analysis of an organic compound (A) of formula C_xH_yO shows that the % by mass of oxygen is 21.62% and the ratio of the mass of carbon in (A) to that of hydrogen is 4.8.

A) <u>Molecular formula and Isomerism:</u>

1) Show that the molecular formula of (A) is $C_4H_{10}O$.
2) Write all possible isomers of (A).

B) <u>Identification of an alcohol by an esterification reaction:</u>

0.2 mol of the compound (A) and a volume V_2 (ml) of ethanoic acid undergo reflux heating for 30 min in presence of 1 ml of concentrated sulfuric acid and 2 – 3 boiling stones. After 30 min the mixture reaches equilibrium where 0.08 mol of ethanoic acid are left.

Given: $\int_{(acid)}$ = 1.05 g/ml ; $M_{(acid)}$ = 60 g/mol

1) Write the general equation of esterification reaction.
2) Determine the value of V_2 if the mixture of alcohol and ethanoic acid is equimolar.
3) Calculate the % yield of the reaction.
4) Identify the alcohol (A) used in esterification reaction.
5) Determine the mol composition of the system at equilibrium.

C) <u>Study of the esterification reaction:</u>

In a second experiment 2 mol of alcohol (A) and 1 mol of ethanoic acid are mixed with each other. The mixture is heated for one hour, the number of moles of ester is 0.6 mol.

1) Write the equation of esterification reaction.
2) Name the ester obtained.
3) Determine the % yield of the reaction.
4) Verify whether the heating duration (one hour) was sufficient to reach equilibrium.
5) Suggest two experimental ways that help to increase yield of the reaction.

Solution

Organic compound: C_xH_yO

% by mass (O) = 21.62%

Ratio of the mass of carbon to that of hydrogen is 4.8

A) 1) * % by mass (O) = $\dfrac{M_{(O)}}{M_{(compound)}} \times 100$

$$21.62 = \frac{16}{12x + y + 16} \times 100 \qquad \text{eq (1)}$$

$$* \ \frac{M(C)}{M(H)} = 4.8 \Rightarrow \frac{12x}{y} = 4.8 \Rightarrow 12x = 4.8y \qquad \text{eq (2)}$$

Substitute eq (2) in eq (1)

$$21.62 = \frac{1600}{4.8y + y + 16}$$

$21.62(5.8y + 16) = 1600 \Rightarrow 5.8y + 16 = 74$

$5.8y = 58 \Rightarrow y = 10$; $12x = 4.8y \Rightarrow x = 4$

M.F of (A): $C_4H_{10}O$

2) Isomers of (A)

$CH_3 - CH_2 - CH_2 - CH_2 - OH$

1 – butanol

$$\begin{array}{l} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3 \end{array}$$

2 – butanol

$$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - OH$$

2 – methyl – 1 – propanol

$$CH_3 - \overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - CH_3$$

2 – methyl – 2 – propanol

B) 0.2 mol of (A) + ethanoic acid □ 0.08 mol of acid left

1)

$$ROH + R' - \overset{\displaystyle O}{\overset{\|}{C}} - OH \ \square \ R' - \overset{\displaystyle O}{\overset{\|}{C}} - OR + H_2O$$

2) n (A) = n (acid)

$$0.2 = \frac{m_{(acid)}}{M_{(acid)}}$$

$$0.2 = \frac{\int \times V_{(acid)}}{M_{(acid)}} \Rightarrow 0.2 = \frac{1.05 \times V_2}{60} \Rightarrow V_2 = \frac{0.2 \times 60}{1.05} = 11.4 \text{ ml}$$

3) Alcohol (A) + acid ⇌ Ester + H_2O

	Alcohol (A)	acid	Ester	H_2O
t = 0	0.2 mol	0.2 mol	0	0
t = t	0.2 – x	0.2 – x	x	x

At time t: 0.2 – x = 0.08 ⇒ x = 0.12 mol

$$\% \text{ yield} = \frac{n \text{ act}}{n \text{ th}} \times 100$$

n act = x = 0.12 mol

Assume that the reaction is complete:

$$\frac{n \text{ (ester th)}}{1} = \frac{n \text{ (alcohol)}}{1} = 0.2 \text{ mol}$$

$$\% \text{ yield} = \frac{0.12}{0.2} \times 100 = 60\%$$

4) Starting from an equimolar mixture of alcohol and acid, the % yield = 60%.

∴ The alcohol is a secondary alcohol.

(A) Is 2-butanol

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$$

5) At equilibrium: n (alcohol) = n (acid) = 0.2 – x = 0.2 – 0.12 = 0.08 mol

n (ester) = n(H_2O) = x = 0.12 mol

C) 2 mol of (A) + 1 mol of ethanoic acid

1)

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 + CH_3-\overset{\overset{O}{||}}{C}-OH \rightleftharpoons CH_3-\overset{\overset{O}{||}}{C}-O\ \underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 + H_2O$$

2) (E): 1-methyl propyl ethanoate

3) Alcohol + acid ⇌ Ester + H_2O

	Alcohol	acid	Ester	H_2O
t = 0	2 mol	1 mol	0	0
t = t	2 – x	1 – x	x	x

At time t: n (ester) = 0.6 mol ; x = 0.6 mol

$$\% \text{ yield} = \frac{\text{n act}}{\text{n th}} \times 100 \Rightarrow \text{n act} = x = 0.6 \text{ mol}$$

Assume that the reaction is complete:

$$\frac{\text{n (ester th)}}{1} = \frac{\text{n (acid)}}{1} = 1 \text{ mol}$$

$$\% \text{ yield} = \frac{0.6}{1} \times 100 = 60\%$$

4) The heating duration wasn't sufficient to reach equilibrium since for an equimolar amount of a secondary alcohol and acid at equilibrium the % yield = 60% but in the above experiment the mixture isn't equimolar. The % yield must be greater than 60%.

5) Using a mixture of reactants which isn't equimolar $\Rightarrow$ forward reaction is favored $\Rightarrow$ % yield increases.

   Using H_2SO_4 in large amount, it acts as a dehydrating agent $\Rightarrow$ it eliminates water $\Rightarrow$ forward reaction is favored $\Rightarrow$ % yield increases.

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Exercise: 13 **Analysis of organic compounds**

An organic compound (A) contains carbon, hydrogen and oxygen. The % composition by mass of each element in the above compound is: % C = 40 % % H = 6.66 %

A) Molecular Formulas

1) Determine the empirical formula of compound (A).
2) Show that the molecular formula of compound (A) is $C_2H_4O_2$ if the molar mass of (A) is 60 g/mol.
3) **(A) is obtained by continuous mild oxidation of an organic compound (B).**
   a) Determine the molecular formula of (B).
   b) Write the condensed structural formula of (B). Name its functional group.

B) Reaction between (A) and (B)

We mix 28.57 mL of (A) and 29.11 ml of (B) and few drops of concentrated sulfuric acid, the following reaction takes place.

$$\text{(A)} + \text{(B)} \rightleftarrows E + H_2O$$

At equilibrium the number of moles of ester formed is 0.33 mol.

Given:

Compounds	(A)	(B)
Density g/mL	1.05	0.79
Molar mass in g/mol	60	46

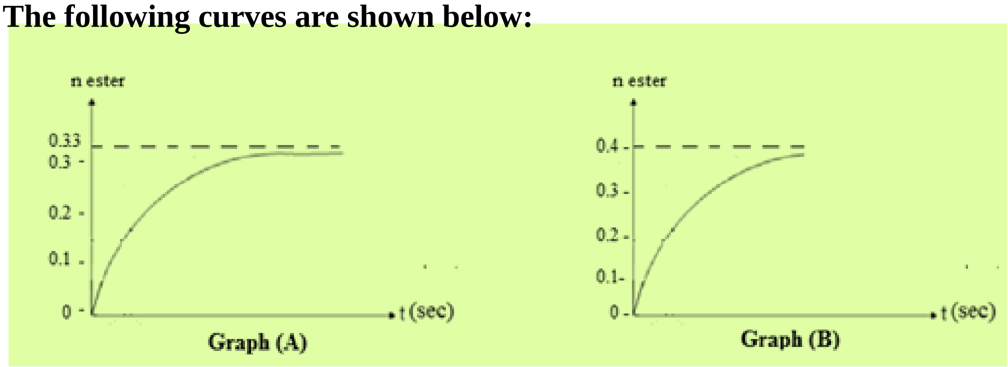
1) Write the equation of the reaction between (A) and (B).
2) Show that the initial reactants are equimolar.
3) Calculate the degree of conversion of (A) at equilibrium
4) Determine the % yield of the above reaction
5) Verify if the yield would increase upon increasing the temperature.

C) Experimental study

Two experiments are performed under the same conditions where their initial states are given in the following table:

Experiments	n A	n B	n E	n H_2O
1	0.5	0.5	0	0
2	1	0.5	0	0

The following curves are shown below:



1) Associate by justifying your answer each one of the curves (A) and (B) with the corresponding experimental condition.
2) Draw a conclusion.

Solution

A)

1) %C = 40% %H = 6.66% %O = 100 –(40+6.66) = 53.34%

In 100g compound:

$$\left.\begin{array}{l} n\,(C) = \frac{\%\,(C)}{M\,(C)} = \frac{40}{12} = 3.33 \\ n\,(H) = \frac{\%\,(H)}{M\,(H)} = \frac{6.66}{1} = 6.66 \\ n\,(O) = \frac{\%\,(O)}{M\,(O)} = \frac{53.34}{16} = 3.33 \end{array}\right\} \begin{array}{l} \frac{3.33}{3.33} = 1 \\ \frac{6.66}{3.33} = 2 \\ \frac{3.33}{3.33} = 1 \end{array} \qquad E.F: CH_2O$$

2) $(E.F)_x = M_{cpd}$

M = 60 g/mol

$(CH_2O)_x = 60 \longrightarrow 12x + 2x + 16x = 60 \longrightarrow 30x = 60 \longrightarrow x = 2$

Molecular formula: $C_2H_4O_2$

3) a) $B + O_2 \rightarrow C_2H_4O_2$

Let (B) be $C_xH_yO_z$

$C_xH_yO_z + O_2 \rightarrow C_2H_4O_2 + H_2O$

According to the law of conservation of atoms, the total number of atoms in the reactants is equal to the total number of atoms in the products.

w.r.to carbon: $x = 2$ w.r.to hydrogen: $y = 4 + 2 \rightarrow y = 6$

w.r.to oxygen: $Z + 2 = 3 \rightarrow Z = 1$

The molecular formula of (B) is C_2H_6O

b) The condensed structural formula of (B) is $CH_3 - CH_2\ OH$.

Its functional group is the hydroxyl group.

B) 1) $CH_3COOH + CH_3CH_2OH \rightleftarrows CH_3COOCH_2CH_3 + H_2O$

2) n (A) = $\frac{m}{M} = \frac{\rho \times V}{M} = \frac{1.05\ g/ml \times 28.57\ mL}{60} = \frac{30}{60}$= 0.5 mol

n (B) = $\frac{m}{M} = \frac{\rho \times V}{M} = \frac{0.79\ g/ml \times 29.11\ mL}{46}$= 0.5 mol

The initial reactants are equimolar

3)

	(A)	+	(B)	⇄	(E)	+	H_2O
t = 0	0.5		0.5		0		0
t: t_{eq}	0.5 – x		0.5 – x		x		x

At equilibrium: n ester = x = 0.33 mol $\alpha = \frac{\text{n dissociated}}{\text{n initial}} = \frac{0.33}{0.5}$ = 0.66

4) % yield = $\frac{\text{act mole}}{\text{theo mole}} \times 100$

Actual mole = x = 0.33

Assume that reaction is complete:

n (E) = n (A) = 0.5 mol ⟶% yield = $\frac{0.33}{0.5} \times 100$ = 66 %

5) Upon increasing the temperature, the yield of the reaction isn't affected since the reaction is athermic.

C) 1) Graph (A) corresponds to experiment (1) since when the initial mixture of reactants is of 0.5 mol, the number of moles of ester is 0.33. While graph (B) corresponds to experiment (2), since the initial mixture of the reactants isn't equimolar

2) Using mixture of reactants which isn't equimolar increases the yield of esterification reaction.

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