Ch(11) : Carboxylic acids and derivatives

I- Introduction

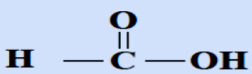
Carboxylic acids are organic compounds of general formula $C_nH_{2n}O_2$, they are characterized by the presence of carboxyl group (-COOH).

Carboxylic acids are liquid or solid at room temperature, their boiling points increase as the number of carbon (n) increases.

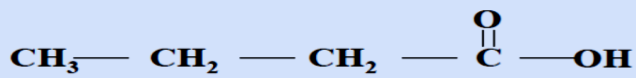
Carboxylic acids change the color of litmus paper from blue to red.

II- IUPAC names of carboxylic acids

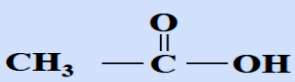
The names of carboxylic acids are derived from the names of alkanes with addition of the suffix (oic acid)



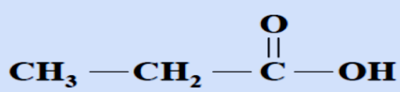
Methanoic acid (CH_2O_2)



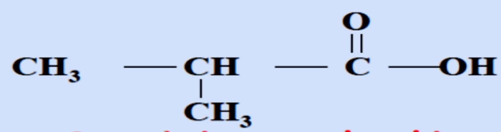
Butanoic acid (butyric acid) ($C_4H_8O_2$)



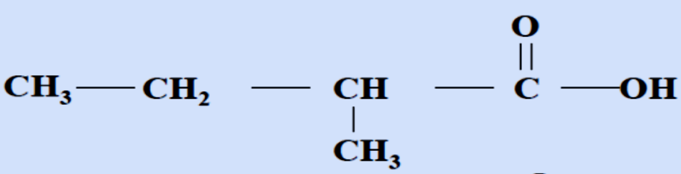
Ethanoic acid (acetic acid) ($C_2H_4O_2$)



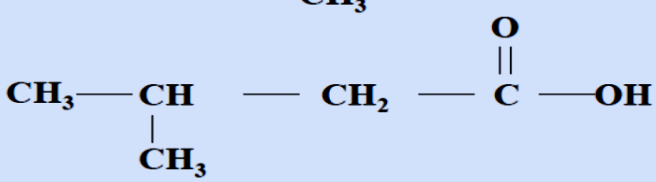
Propanoic acid ($C_3H_6O_2$)



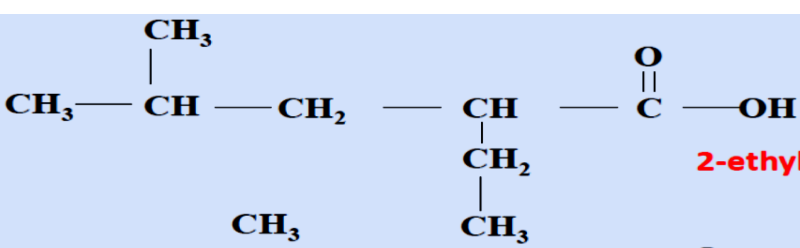
2-methylpropanoic acid or methylpropanoic acid ($C_4H_8O_2$)



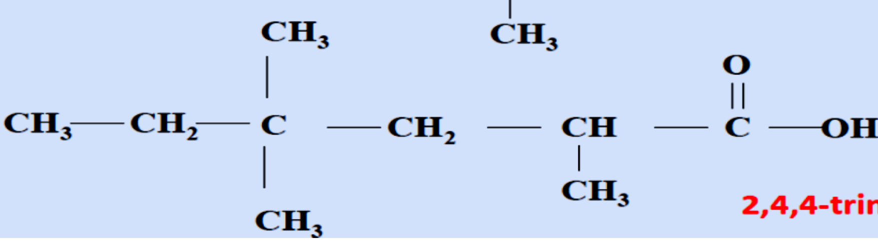
2-methylbutanoic acid



3-methylbutanoic acid



2-ethyl-4-methylpentanoic acid ($C_8H_{16}O_2$)



2,4,4-trimethylhexanoic acid ($C_9H_{18}O_2$)

IV- Carboxylic acid derivatives

Carboxylic acid derivatives are compounds in which the (OH) of carboxylic acid is replaced by an atom or group of atom (Z) according to the following equation :

$$R-\overset{\overset{\large O}{||}}{C}-OH + X\text{-}Z \rightarrow \underbrace{R-\overset{\overset{\large O}{||}}{C}-Z}_{\text{Carboxylic acid derivative}} + X-OH$$

The three important carboxylic acid derivatives are : Acylchloride , acid anhydride and esters.

3. Esters ($C_nH_{2n}O_2$)

Esters are prepared by the reaction of carboxylic acids with alcohols according to the following equation (it is called reaction of synthesis of ester):

$$R-\overset{\overset{\large O}{||}}{C}-OH + R'-OH \rightleftarrows R-\overset{\overset{\large O}{||}}{C}-O-R' + HOH\ (H_2O)$$

$$C_nH_{2n}O_2 + C_{n'}H_{2n'+2}O \rightleftarrows C_{n''}H_{2n''}O_2 + H_2O$$

Where n'' = n + n' (the number of atoms is conserved during a chemical reaction)

This reaction is slow, reversible and athermic.

Diluted sulfuric acid (H_2SO_4) is used as catalyst to accelerate this reaction.

IUPAC names of esters

The name of ester = alkyl alkanoate

Alkyl : name of the part coming from alcohol

Alkanoate : name of the part coming from the carboxylic acid

Examples

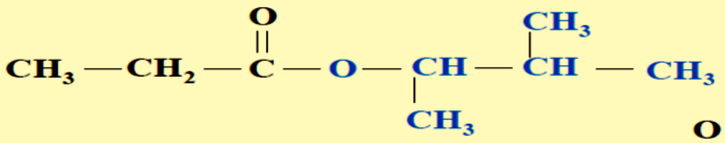
$CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-O-CH_3$ Methyl propanoate

$CH_3-\overset{\overset{\large O}{||}}{C}-O-CH_2-CH_3$ Ethyl ethanoate

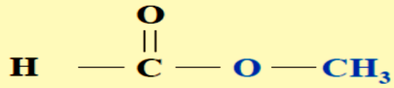
$CH_3-\underset{\underset{\large CH_3}{|}}{CH}-\overset{\overset{\large O}{||}}{C}-O-CH_2-CH_3$ Ethyl-2-methyl propanoate
Or ethyl methylpropanoate

$CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-O-\underset{\underset{\large CH_3}{|}}{CH}-CH_3$ 1-methylethyl propanoate

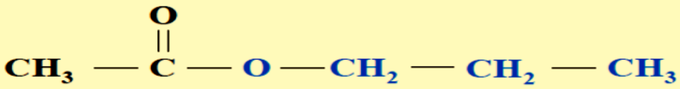
$CH_3-\underset{\underset{\large CH_3}{|}}{CH}-\overset{\overset{\large O}{||}}{C}-O-\underset{\underset{\large CH_3}{|}}{CH}-CH_3$ 1-methylethyl-2-methylpropanoate



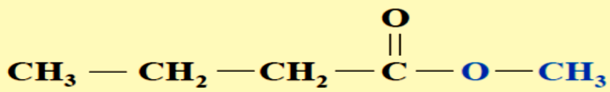
1,2-dimethylpropyl propanoate



Methyl methanoate



propyl ethanoate



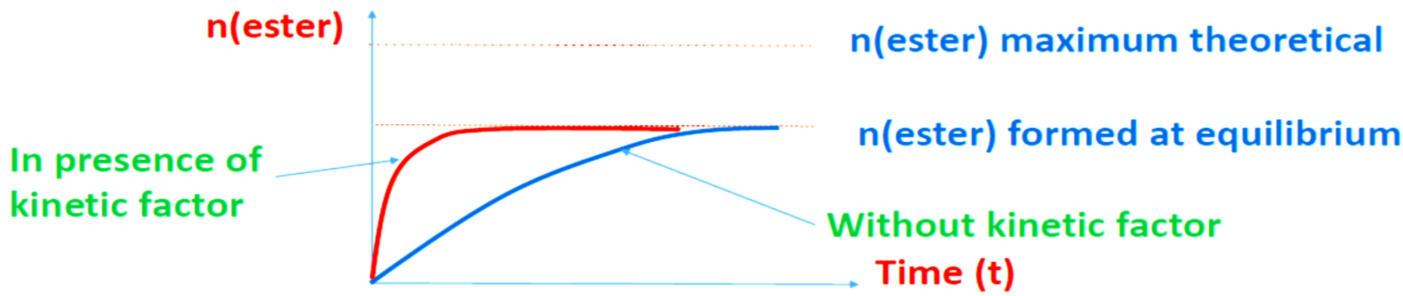
Methyl butanoate

Effect of kinetic factors on the esterification reaction

Since the esterification is a slow reaction, we use two kinetic factors to accelerate this reaction :

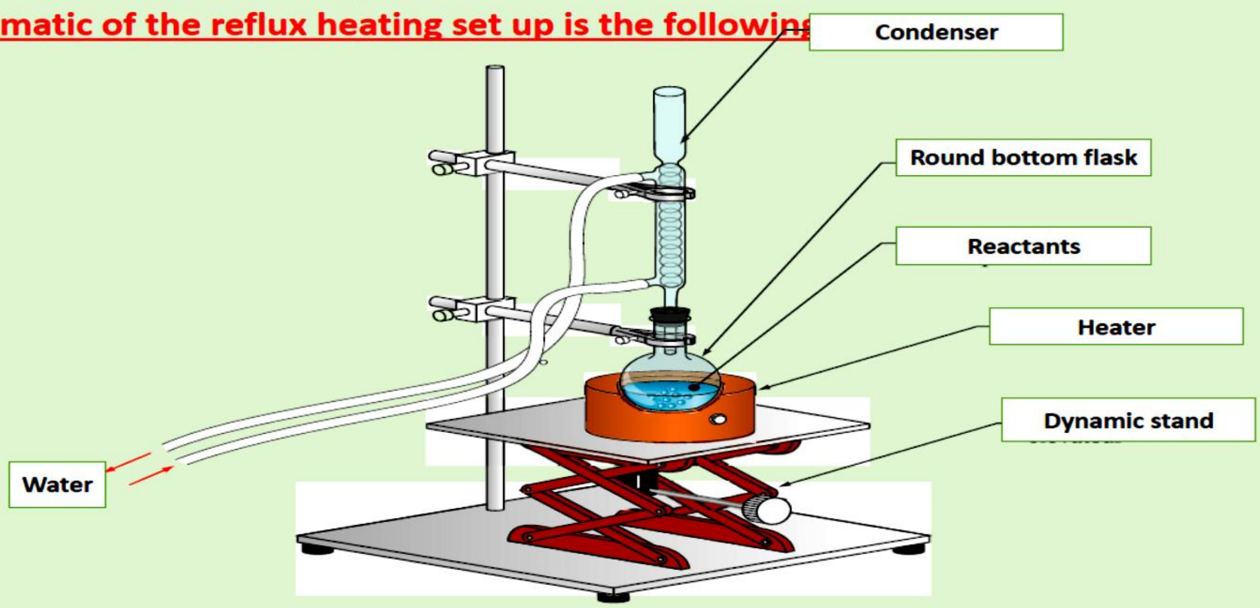
1. **The heating of the system (increase of temperature).**
2. **The use of diluted sulfuric acid as catalyst.**

These two factors accelerate the reaction to reach its equilibrium state faster without change in the equilibrium state (the amount of ester formed at equilibrium remains the same as indicated in the following graph :



The heating of reactants is carried out under reflux in the purpose to prevent the loss of reactants as form of vapors.

The schematic of the reflux heating set up is the following:



Yield of esterification reaction

Generally, the yield of esterification of carboxylic acids with primary alcohols is about 67 % if we use an equimolar mixture (stoichiometric) of carboxylic acids with alcohols.
Since the esterification reaction is athermic, thus we cannot change the constant K_c by change of temperature and therefore we cannot increase the yield by increase of temperature.

How to increase the yield of esterification reaction?

To increase the yield of esterification, two ways are possible :

1. We use an initial non equimolar mixture of reactants (carboxylic and alcohol) where we use a large excess of one of the reactant which allows the reaction to produce more products and to readjust its equilibrium constant.
2. We use a large amount of catalyst H_2SO_4 (concentrated solution), in this case sulfuric acid plays a role of dehydrating agent that absorbs the water formed from the reaction and allows the reaction to produce more products in the purpose to readjust its equilibrium constant.