COURSE GUIDE

SED 222
GENERAL CHEMISTRY FOR INTEGRATED SCIENCE II

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INTRODUCTION

Welcome to this chemistry course. We suppose that many of you are taking this course because you want to strengthen your-background in chemistry. Armed with this strong background in chemistry, you can then proceed to advanced programmes in chemistry. The training of biologists, geoscientists, medical doctors, nurses, soil scientists, food scientists, chemical engineers, petroleum engineers and many others requires that students in those areas have a good exposure in chemistry.

We have packaged this chemistry course in such a way that you will learn chemistry using a technique peculiar to the open learning system. This technique has been adopted by the National Open University of Nigeria in most of the courses offered to students.

You will here learn the content of this chemistry course at a reasonable pace. You will need to master the language chemists use to describe the world around us. The language is simple, interesting and specific to the subject, chemistry.

We wish you success with the course and hope that you will find it both interesting and useful.

WHAT YOU WILL LEARN IN THIS COURSE

This course is titled “General Chemistry for Integrated Science I" this present course, you will be presented information in chemistry in a structured way to make learning easier. All the units follow the same pattern and so after the first few units, the rest will become easy to follow.

LEARNING OUTCOMES-AIMS AND OBJECTIVES

The broad aims of this foundation chemistry course can be summarized thus. The course aims to provide you with chemistry content that will be sufficient for you in the integrated science program. Thus you will have solid foundation in chemistry which will enable you go into an advanced science course needing a background of chemistry.

The objectives of this course are set out below. On completion of the course, you should be able to:

1) Distinguish between chemistry and the other science subjects.
2) Discuss the role of chemistry in our everyday living.
3) Apply the language of chemistry in describing the world around you.
4) Carry out simple chemical calculations.

MAIN CONTENT

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MODULE 1

UNIT 1 INTRODUCTION TO ORGANIC CHEMISTRY AND CLASSIFICATION OF ORGANIC MOLECULES

CONTENTS

1.0 INTRODUCTION

You should have read through the Course Guide on Organic Chemistry. If so, you will have noticed that organic chemistry is essentially the chemistry of carbon compounds However, if this was not apparent from the Course Guide, we can define organic chemistry as the study of carbon compounds. Organic chemistry owes its name to the fact that the original compounds studied came from living things plants or animals The term "organic" means things formed from living things. Over time, the study of organic chemistry has expanded to include other compounds other than the so-called organic compounds e.g. plastics, which have no direct relation to living matter. Nevertheless, organic chemistry is retained as the umbrella name for the study of compounds of carbon, irrespective of its origin, but excluding the oxides of carbon. Apart from carbon, organic compounds, may contain one or more other elements e.g. hydrogen, oxygen, nitrogen, sulphur and the halogens.

The scope of organic chemistry is very' large, millions of organic compounds have been isolated or prepared, yet the number 'of guiding principles is relatively snail. The continuing interest and importance of organic chemistry starts from the fact that organic compounds are essential for the sustainance of life e.g. carbohydrates, proteins, fats and oils etc. Modern civilization consumes vast quantities of organic compound. Coal, petroleum, and natural gas are primary sources of carbon compounds for use in production of energy and as starting materials for the preparation of plastics, synthetic fibers, dyes, pesticides, fertilizers, detergents, rubbers, paints, medicines and drugs, perfumes and flavours.

I hope you now appreciate the importance of the subject organic chemistry and the relevance of organic compounds to us.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- state the distinct nature of organic chemistry.
- define organic chemistry.
- explain the uniqueness of carbon as a building block for organic compounds.

3.0 MAIN CONTENT

3.1 Definition and Scope of Organic Chemistry

Organic Chemistry is the study of the chemistry of carbon compound, which apart from carbon, m contain one or more of hydrogen, oxygen, nitrogen, sulphur and any of the halogens. Carbon compounds are .00data in nature all well over 50% of all known compounds. All living organisms comprised of, manufac$_{re}$ and consumes organic or carbon compounds. Millions of organic compounds are known and the pote$_{al}$ to identify or prepare millions of such compounds is real. Organic compounds are found in and essential aspects of our lives.

Recall the impact of organic compounds in our day-to-day living as enumerated in the introductory sect$_{n}$ to this unit.

3.2 Uniqueness of Carbon Atom

We had earlier defined organic chemistry as the study of the compounds of carbon. Why is so much chemistry centred on a single element, carbon? Carbon is so unique amongst the elements, in that its known compounds are much more numerous than the known compounds of all the other 105 elements put together. Carbon atom is an element which has six electrons with four in the outermost orbit; and is placed in period 2 and Group 4 of the Periodic Table. The uniqueness of carbon atom gems from its ability to form:

i. a variety of strong covalent carbon-carbons bond
ii. (Li) long chains or rings of carbon atoms bonded to one another called CATENATION.
iii. strong covalent bonds with other elements
iv. multiple bonds (double and triple) with another carbon atom or other elements.

Examples of such bond forming ability are. (Fig. I .1)

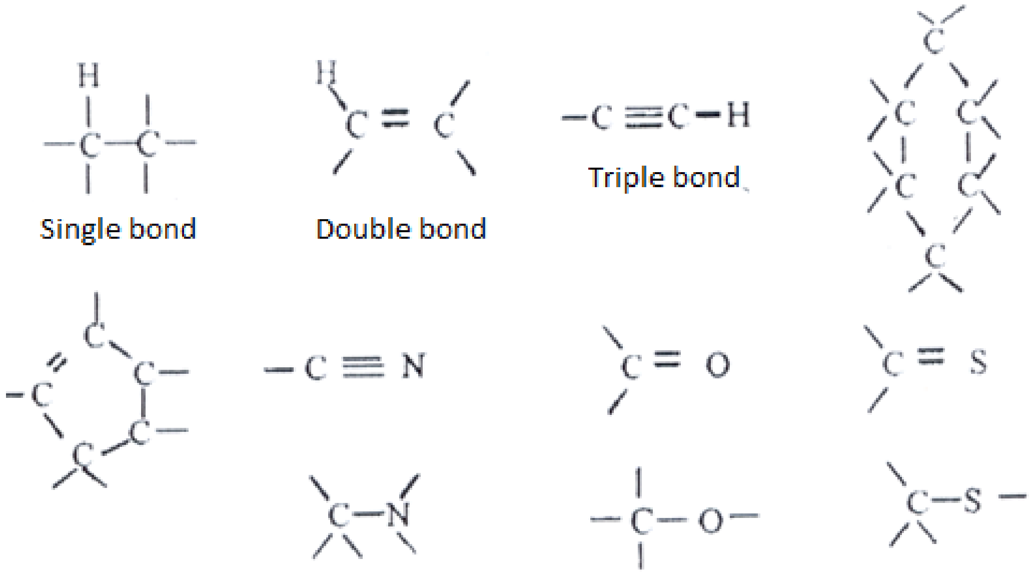


Fig. 1:1 Types of covalent bonds formed by carbon

In all these bonds, carbon shows a valency of four. The special properties of carbon can be attributed to its being a relatively small atom with four valence electrons. The energy changes involved in gaining or losing four electrons, to form a stable configuration, are very high so that simple C^4 f and C^{4-} ions do not exist, but customarily, carbon completes its valence-shell octet by sharing electrons (covalent bond formation) with other atoms (carbon or other elements).

SELF ASSESSMENT EXERCISE

1) Dine catenation.
2) pt the four features that make carbon unique in its bond forming ability.
3) Thy does carbon form covalent bonds and not ionic bonds?

1. Representation of Organic Molecules

From our discussion so far, it should be clear that carbon forms three types of covalent bonds – single - double and triple bonds with either itself or with other elements. Covalent bonds are directed in space (spatial arrangement) so that molecules containing them may be three-dimensional; as for CH_4 (methane). It is not easy to represent such spatial arrangement on paper but look at the model below.

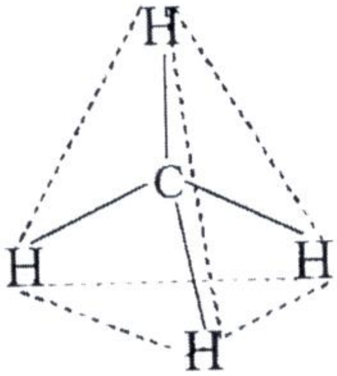
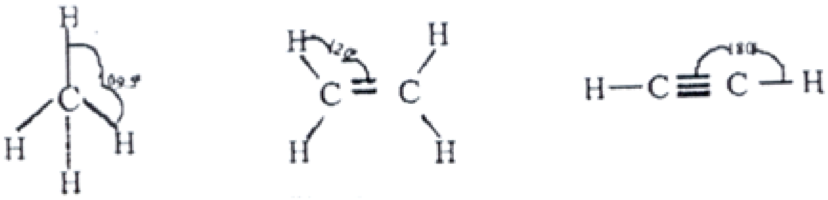


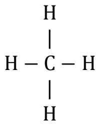
Fig. 1:2 Three-dimensional structure of the molecule CH_4

The four single covalent bonds around carbon if equivalent, are arranged at the corners of a tetrahedron (Fig. 1.3(0) with the H–C–H bond angles of 109°. In molecules, e.g. ethene, C_211_4, in which the carbon atom is surrounded by two single and one double bond, such a molecule is planar (Fig. 1.3(11)) with bald angle of 120^0. For molecules e.g. ethyne, C_2f1_2, in which the carbon atom is surrounded by one single and one triple bond, such molecule is collinear (Fig. 1.3(iii)) with bond angles of 180^0.



(1) tetrahedron (ii) planar (iii) collinear

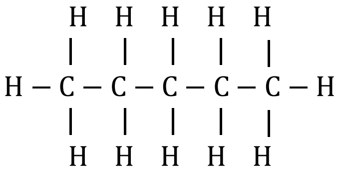
Fig. 1,3: Directional nature of bonds formed in simple molecules

On paper, either the molecular formula e.g. CH_4 or planar structural formula  $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$ can be used for representing molecule. It is easy when reading a book to come to regard all organic molecules as being flat; it is important to remember that most of them are not.

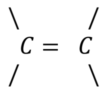
3.3 Classification of Organic Compounds

You will recall that in this unit, it was mentioned that organic compounds are numerous. However, the number of guiding principles is relatively small; one of such principles is the classification of organic compounds as shown in Fig 1.4.

3.3.1 Open-Chain or Aliphatic Compounds

These are compounds that contain chains of interlinked carbon atoms (may involve other eleme), The chains length varies over a wide range of carbon atoms e.g. Pentane, C_5H_{12}  $\begin{array}{ccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$

3.3.2 Saturated and unsaturated compounds

When all the bonds between the carbon atoms (may involve other elements) are single, the compound is salt to be saturated e.g. Pentane. If, however, multiple bonds e.g. the double bond in alkenes  and triple bond in alkynes $- C \equiv C -$ is present in the molecule, the compound is said to be unsaturated.

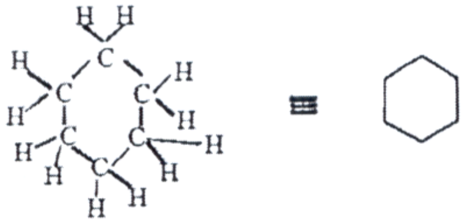
3.3.3 Aromatic Compound

These are carbocyclic compounds endowed with what is referred to as aromatic character i.e. they contain rings of carbon atoms, based on benzene C_6A_6; (Unit 7) which can be represented as shown below

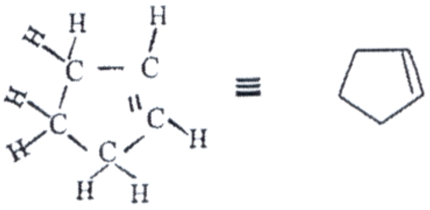
There are important differences in properties between aliphatic and aromatic compounds, e.g. between hexane $C_6 1^{-}1_{12}$ and benzene, $C,_5 11_6$.

3.3.4 Alicyclic Compound

These are carbocyclic compounds with C-C and/or C = C bonds between the carbon atoms in the ring. Benzene is not normally classified as alicyclic even though it is carbocyclic. The reasons for this will be explained in Unit 7. Compounds in this group have some properties similar to those of aliphatic compounds; hence the name alicyclic.



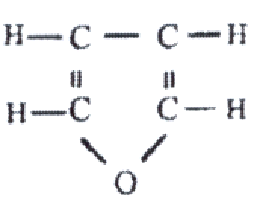
Cyclohexane



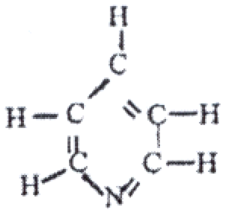
cyclopentene

3.3.5 Heterocyclic compounds

These are cyclic compounds containing elements other than carbon, particularly oxygen, nitrogen or sulphur in the ring e.g.



Furan



Pyridine

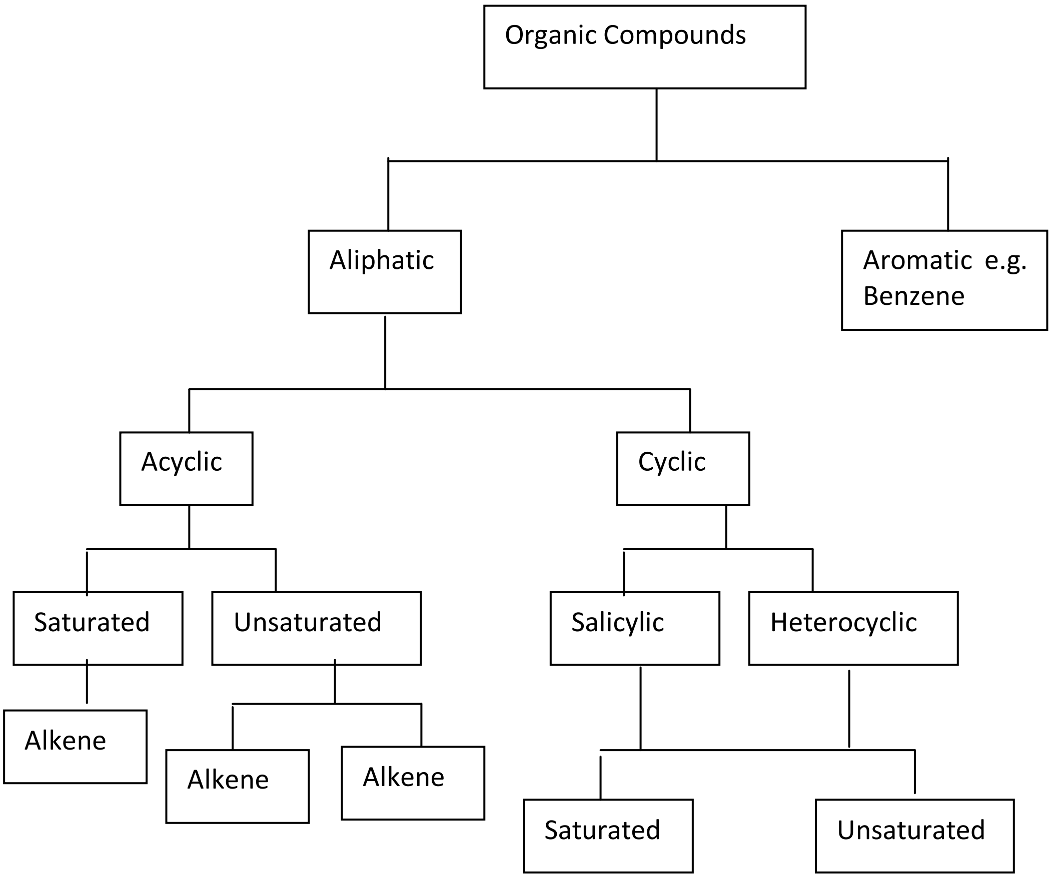


Fig. 1.4: Classification of organic compounds

4.0 CONCLUSION

In this unit you have learned about organic chemistry as the study of carbon compounds. These compounds are abundant in nature and they play important roles in our life. Carbon is able to firm such vast amount of compounds because of its ability to covalently bond with carbon atoms and other elements in chains of ring forms. The vast numbers of carton compounds makes it necessary to classify them into groups of compounds with similar characteristic for easy comprehension.

5.0 SUMMARY

You have learnt in this unit the definition of organic chemistry and about organic compounds. This has served to introduce you to the nature and scope of organic chemistry, as well as the special position of carbon atom in organic compounds. The classification of these compounds shall form the frame work for our discussion in subsequent unit.

6.0 TUTOR-MARKED ASSIGNMENT

Briefly explain the features that enable carbon atoms to form vast amount of organic compounds.

7.0 REFERENCES/FURTHER READING

Brown, GA (1978). *An Introduction to Organic Chemistry*. Lagos: Longman Publishers.

UNIT 2 THE HOMOLOGOUS SERIES, FUNCTIONAL GROUPS AND ISOMERISM

CONTENTS

1.0 INTRODUCTION

You have been introduced to organic chemistry in Unit 1 and now that you are aware of the scope of this section of chemistry; you will learn in this unit some important concepts or terminologies commonly used in organic chemistry. The terms homologous series and functional groups explain some of the umbrella principles that help in the understanding of organic compounds despite their large number. Isomerism explains the existence of organic compounds having the same number and kind of atoms but showing differing characteristics due to the differences in the way the atoms are arranged within the molecules.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define the terms homologous series, functional groups and isomerism.
- list the characteristics of a homologous series,
- identify the structural representation of simple organic functional groups.
- draw and name the structural isomers of hydrocarbon compounds having a maximum of five carbon atoms.
- distinguish between structural and geometrical isomerism.

3.0 MAIN CONTENT

3.1 The Homologous Series

In unit 1 you learned that organic compounds are numerous in number, in fact, they are in millions. In dealing with such large number of compounds, some form of classification is essential as was exemplified in unit 1. It was observed that certain set of compounds show structural, physical and chemical similarities and are said to constitute a homologous series. A homologous series can be defined as a collection of a small number of series of organic compounds with unique structural pattern and properties, each member differs by a constant - CH_2 - unit. The term homologous is used to describe a group of compounds with the following characteristics:

(i) they can be prepared by similar methods;
(ii) they have similar chemical properties;
(iii) there is a regular gradation of physical properties (melting or boiling points, solubility);
(iv) they can be represented by a general formula e.g. C_nH_{2n+2} for alkanes; C_nH_{2n} for alkenes, C_nH_{2n-2} for alkenes, C_nM_{2n-2} for alkynes, $C_uH_{2N+1}OH$ for alkanols, $C_nH_{2n+1}COOH$ for alkanoic acids;
(v) each member differs in molecular formula from the preceeding compound by –CH_2- (mass unit of 14) e.g. in alkanes, CH_4, C_2H_6, C_3 H_8, C_4H_{10}, etc.
(vi) each member contains at least one functional group e.g. C=C for alkene, C≡C for alkynes, -OH for alkanols, -COOH for allcanoic acid.

These characteristics are very essential for the understanding of organic chemistry and will be encountered throughout your study of organic chemistry.

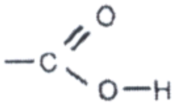
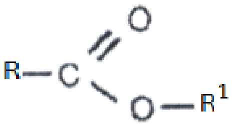
SELF-ASSESSMENT EXERCISE

Write the structure of the first 10 members of the alkane homologous series.

3.1 Functional Groups

One of the characteristics of a homologous series you learned in Section 2.2 of this unit, is that each member of a series contains at least one functional group. In fact, the functional group determines the properties of a homologous series. A functional gram is a structural feature consisting of atoms or bonds found in organic compounds that control the classification and reactivity of the molecules. The study of organic chemistry becomes simplified when examined according to their functional grams. One of the main reasons for classifying compounds by their functional groups is that it also classifies their chemical behaviour and, to sane extent, their physical properties. Table 2.1 summarizes sane of the commonest functional groups.

Table 2.1 Classification of Simple Organic Compounds by Functional Groups

Class of Compounds	**Functional Group**	**Suffix**	**General Representation**	**Example**
Alkanes	-C-C- bond	-ane	RH or R—R	ethane
Alkenes	-C=C- bond	-aie		ethene
Alknes	-C≡ bond	-yne		ethyne
Allcanols (alcohols)	-0-H	-al	R-OH	ethanol
Alkanoic acids . (carboxylic acids)	 or -COOH or -CO_2H	-oic acid	R-COOH	ethanoic acid
Alkanoates (esters)		-oates	R-$0O_3H^1$	ethyl ethanoate
Alkananine (Amine)	-NH_2	-amine	R-NH_2	ethanamine

Note: At' in organic chemistry represents an alkyl group or radical which is an aflame less one hydrogen atom.

The number of common functional groups is small in comparison with the total number of organic compounds. The contents of organic chemistry are therefore, arranged together lithe emphasis is put on the characteristics of individual functional groups. Once these properties e.g. method of preparation, chemical reactivity, etc. have been illustrated it is possible, with reasonable accuracy, to predict the properties of any compound containing such functional groups. This is what makes the study of organic chemistry simple despite the large number of compounds involved.

3.2 Isomerism

This is the term used to describe the existence of two or more organic compounds with the same molecular formula, but different structural formulae. The different forms of the compounds are called isomers and have different chemical and physical properties.

$$\begin{array}{c} molecular \\ formula \end{array} C_2H_4O \Rightarrow \begin{array}{c} structural\,formula\;of\;isomers \\ CH,-O-CH \quad CH-CH-OH \end{array}$$

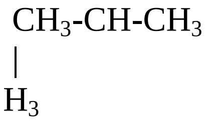
Stated in another way, compounds having the same number and kind of atoms but the atoms are arranged differently are called isomers. Your left and right hands contain the same features but arranged differently; they are isomers of one another. What about your pair of shoes?

Activity: Look around you and see how many pairs of isomers you can recognise. There are two types of isomerism that are known to exist in organic compounds - structural isomerism and stereoisomerism is also known as Geometric isomerism.

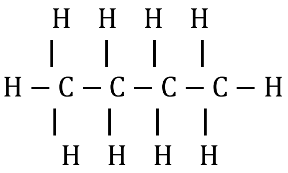
3.2.1 Structural Isomerism

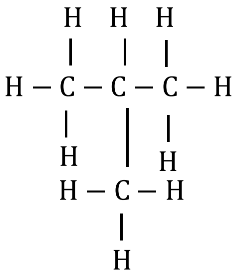
In structural isomers the molecules contain the same number of each kind of atom but differ in regard to which atom is linked to which. In structural isomerism the difference arise simply from the arrangement of atoms within the molecule, resulting in two or more different structural formulae.

$CH_3\text{-}CH_2\text{-}CH_rCH_3$



$CH_3\text{-}\underset{\substack{|\\ H_3}}{CH}\text{-}CH_3$

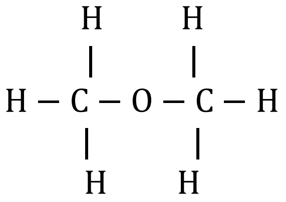




butane C_4H_{10} 2-methylpropane

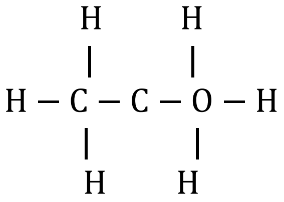
- Consider the words Ronald, Roland, Arnold, they contain the same numbers of the same letters written in such a way to give different words - structural isomers.

The isomers are all separate, distinct compounds and even the names may be different. If they contain the same functional group and are members of the same homologous series e.g. C_4H_{to}. They have many chemical properties in common but have different physical properties. If they contain different functional groups and belong to different homologous series they differ in both chemical and physical properties, e.g. C, H_60



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

methoxymethane



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

ethanol

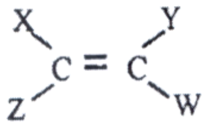
SELF-ASSESSMENT EXERCISE

(a) The first three members of the alkane series, methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) do not exhibit structural isomerism; confirm this by drawing their structural formula yourself

(b) C_4H_{10} has two structural isomers as shown above. The next member of the alkane series C_5H_{12} has three structural isomers.

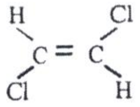
3.2.2 Geometric isomerism

This is a type of isomerism existing in compounds containing double bonds because there is no free rotation of the carbons about double bonds so that these bonds lock the two groups they link in permanent positions.

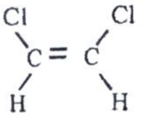


Generally, all alkenes that have two different groups attached to each carbon atom containing the double bond may show geometric isomerisrn. Two arrangements are possible; an isomer in which similar groups are on the same side of the double bond (it is called cis-isomer from the latin word 'same') and the other isomer in which the similar groups are on the opposite sides of the double bond (it is called trans-isomer from the Latin word meaning 'across'). Geometric isomerism is sometimes called cis-nans isomerism.

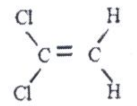
1. $C_2H_2Cl_2$



trans-isomer

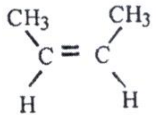


cis-isomer

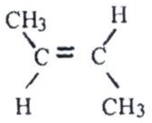


No geometric isomerism.
Can you explain this?

2. C_4H_8

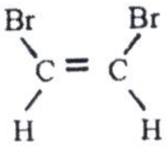


cis-2-butene

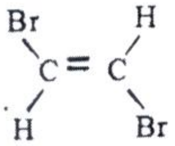


trans-2-butene

3. $C_2H_2Br_2$



cis-1,2-dibromoethene



trans-1,2-dibromoethene

4.0 CONCLUSION

In this unit you have learned about the homologous series and functional groups, two important terms used in organic chemistry to explain the arrangement of organic compounds into a number of chemically similar groups or families. The tents should help you to view organic chemistry as a collection of a set of compounds with similar characteristics rather than the study of all individual compounds. The aim of these classifications therefore is to make the study of the subject matter easy. You have also learned about isomerism which explains the importance of the mode of arrangement of atoms in a molecule and how it could influence the characteristics of the molecules.

5.0 SUMMARY

- What you have learned in this unit concerns the terms homologous series, functional groups and isomerism) as they relate to the study of organic compounds.
- The homologous series is used to describe set of compounds with similar characteristics grouped to ease our understanding of organic chemistry.
- The functional group is the common structural feature in organic compounds that is used for their classification and determines their properties. Isomerism deals with organic compounds having the same number and kind of atoms but structurally different and hence show different characteristics.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Draw all the structural isomers of the compound C_5H_{12}
ii. Draw the cis-trans isomers of C_4H_7C1 (chlorobutene).

7.0 REFERENCES/FURTHER READING

Bajah, S. T., Teibo, B. 0., Onwu G and Obikwere, A. *(2002). Senior Secondary Chemistry* - *Textbook 2* Lagos. Longman Publishers.

Tewari, K. S., Mehrotra V. and Vishnoi, N K. *Textbook of Organic Chemistry.*

UNIT 3 IUPAC NOMECLATURE OF ORGANIC COMPOUNDS

CONTENTS

1.0 INTRODUCTION

In unit 1 you beamed about organic chemistry and the abundance and relevance of organic compounds in nature. You will also recall that the number of known organic compounds are in millions, and continue to increase as more naturally occurring compounds are discovered and many more are prepared. Can you imagine what it takes to remember over a million names? There are so many organic compounds that it is a real problem to provide than all with different, yet sensible, names. It is rather like trying to find different, yet related, surnames for everyone in the world. At the onset of organic chemistry, the names of organic compounds is based on the source from which the compound was obtained or on the structure or properties of the compound. This is known as *trivial system* and the names are called *trivial names* or *common names* e.g.

Trivial Name	*Source*
Urea	Urine
Citric acid	Citrus fruit

This naming system could not be sustained because of the enormous increase in the number of known organic compounds. The new system (or rule) for naming organic compounds, which is now widely accepted, is in accordance with the rules formulated by the International Union of Pure and Applied Chemistry (I UPAC) and is known as *IUPAC System of Nomenclature.* The full set of rules to cover every known compound is complicated. A brief outline is therefore given in this unit and extended throughout the subsequent units.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

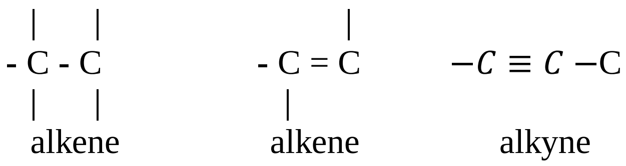
- recall the IUPAC rules for systematic naming of simple organic compounds.
- name the first ten members of each homologous series
- identify the structure of simple organic functional groups and name them using the IUPAC nomenclature

3.0 MAIN CONTENT

3.1 Nomenclature of Organic Compounds

3.1.1 The Hydrocarbons

These are organic compounds consisting of carbon and hydrogen atoms only. There *are three* most important homologous series of hydrocarbons namely alkanes, alkenes and alkynes. Recall the classification of organic compounds as illustrated in Fig. 1.4 of Unit 1; acmes are saturated hydrocarbons while alkenes and alkynes are unsaturated hydrocarbons. Examples of these classes organic compounds are illustrated in Fig. 3.1 below.



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}$ $\qquad -\underset{|}{C}=\overset{|}{C}$ $\qquad -C\equiv C-C$

alkene alkene alkyne

F*ig. 3.1: Examples of three classes of hydrocarbons*

a) Alkanes

The general formula of alkanes is $C_{6}14_{26\cdot 2}$ (where n = whole number). Alkanes are considered to be the parent compound and have the basic formula for writing the structure and name of organic compounds as illustrated in Table 3.1. The alkanes have an -*one* ending (suffix) and the prefix for members of the series is based on the carbon atoms involved. (Table 3.1) *Meth-*, *eth-*, *Prop-* and but - prefixes for the first four members.

The hydrocarbon group formed by the removal of one hydrogen atom from an alkane is called an alkyl group, and is named by dropping 'ane' from the name of the corresponding alkane and adding the suffix `yl as shown in Table 3.1

Table 3:1 1UPAC nomenclature of simple alkanes

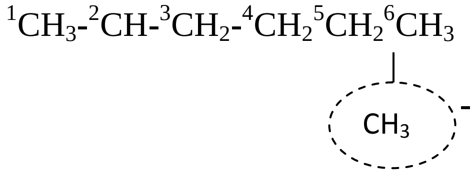
IUPAC NAME	Formula $C.H_{2n3}$	Alkyl group	Formula
Methane	CH_4	Methyl	CH_3
Ethane	C_2H_6	Ethyl	C_2H_5
Propane	$C_3\ H_8$	Propyl	$C_3\ H_7$
Butane	C_4H_{10}	Butyl	$C_4\ H_9$
Pentane	C_5H_{12}	Pentyl	C_5H_{11}
Hexane	C_6H_{14}		
Heptane	C_7H_{16}		
Octane	C_8H_{18}		
Nonane	C_9H_{20}		
Decane	$C_{10}H_{22}$		

SELF-ASSESSMENT EXERCISE

Complete the blank spaces in Table 3.1 following the trend shown for the first five members of the alkane series.

In alkanes with branched (groups not pan of the longest chain of carbon) chains the IUPAC name is based on the number of carbon atoms in the longest chain. This longest chain is then numbered from one end so that the position of the branched chains can be indicated.

The longest chain of carbon atoms can be numbered from either end; the direction chosen is that which enables the lowest numbers to be used. For example:



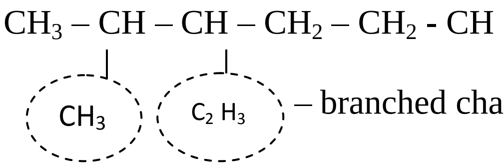
$${}^{1}CH_3\text{-}{}^{2}CH\text{-}{}^{3}CH_2\text{-}{}^{4}CH_2{}^{5}CH_2{}^{6}CH_3$$

$$CH_3$$

- branched chain

2-methylhexane

When two or more branched chains are present they are listed alphabetically.



$$CH_3 - \underset{\substack{|\\CH_3}}{CH} - \underset{\substack{|\\C_2H_3}}{CH} - CH_2 - CH_2 - CH$$

– branched chains

3-ethyl-2-methylhexane

b) Alkenes

The general formula for alkenes is C_nH_{2n} showing that they have two hydrogen atoms less than the corresponding alltanes. Recall the prefixes for the alkanes; which depend on the number of carbon atoms in the organic compound; the same prefixes are retained for the alkenes. However, organic compounds which have double bonds (alkenes) have the suffixes -ate (compare this with the suffixes for alkanes -ane) I guess it is easy to remember. $CH_3 - CH_3$ $CM_2 = CH_2$

ethane, an alkane ethene, an alkene

Table 3.2- IUPAC nomenclature of simple alkenes

ILIPAC Name	*Formula*	*Alkenyl Group*	*Formula*
Ethene	C_2H_4	Ethenyl	$C_2 H_3$ -
Propene	C_3H_6	Properly!	C_3H_5 -
Butene	C_4H_8	Butenyl	C_4H_7 -
Pentene	C_5H_{10}	Pentenyl	$C_5 H_9$-

SELF-ASSESSMENT EXERCISE

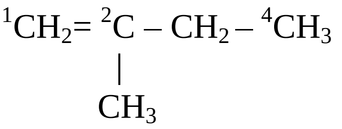
Complete the bank spaces in Table 3.2 using the guide from Table 3.1. The positions of the double bond and of any branched chains are shown by numbering the longest straight chain of carbon atoms. Thus,

$^{1}CH_2= {}^{2}CH^{3}CH_2–-{}^{4}CH_3$

but–1–ene
(not but–3–ene)

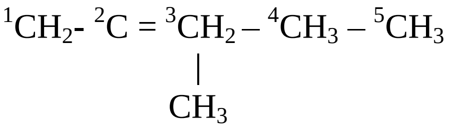
$^{1}CH_3= {}^{2}CH^{3}CH –{}^{4}CH_3$

but–2–ene



$^{1}CH_2= {}^{2}\underset{\underset{\displaystyle CH_3}{|}}{C} – CH_2 – {}^{4}CH_3$

2-methylbut-l-ene
(not 3-methylpent-3-ene)
(not 2-ethylbut-2-ene)



$^{1}CH_2- {}^{2}C = {}^{3}\underset{\underset{\displaystyle CH_3}{|}}{CH_2} – {}^{4}CH_3 – {}^{5}CH_3$

3-methylbut-2-ene)
(not 3-methylpent-3-ene)
(not 2-ethylbut-2-ene)

The hydrocarbon residue formed by the removal of one hydrogen atom from an alkene is called an *alkenyl.* e.g.

$CH_2{=}CH_2 \xrightarrow{H} -CH{=}CH_2$ ethenyl; $CH_3CH = CH_2 \xrightarrow{H} -CH_2CH = CH,$
Ethane propene propenyl

SELF-ASSESSMENT EXERCISE

Can you explain why the names in bracket for the structures above are incorrect?

c) Alkynes

The general formula for alkynes is $C.H_{3n.-2}$. The pattern you learnt for alkanes and alkenes is also used for alkynes except that the suffix cane' for the alkanes is replaced by 'yne' for the alkynes series.

e.g	CH_3 - CH_3	$CH_2{=}CH_2$	$CH{\equiv}CH$
	ethane an alkane	ethene an alkene	ethyne an allcyne

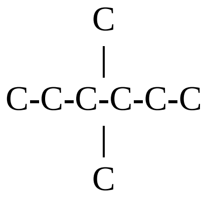
3.1.2 Rules for IUPAC Nomenclature

(a) Introduction

You have been introduced in Section 3.2.1 to the nomenclature of hydrocarbons before been introduced to the rules for the IUPAC nomenclature. This is not an oversight, it is because most organic compounds are considered as derivatives (derived from) of the alkanes formed when the hydrogen(s) of alkanes are replaced *by* various groups or substituents. Thus, the name of any organic compound depends on the correct selection of the parent hydrocarbon or the basic carbon skeleton.

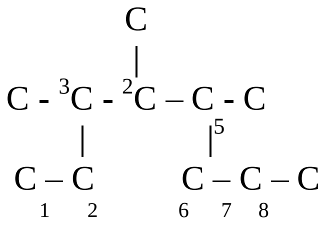
(b) The rules of IU PAC nomenclature
- (i) The first step is to select the longest possible continuous chain of carbon atoms which is called the parent chain.

The parent chain is determined by the number of carbon atoms. All other carbon chains attached to the parents chain are referred to as side chains or substituents. Thus, if the parent chain contains six carbon atoms, the parent hydrocarbon is hexane (structure I)



$$\begin{array}{c} \quad C \\ \quad | \\ C{-}C{-}C{-}C{-}C{-}C \\ \quad | \\ \quad C \end{array}$$

(I)



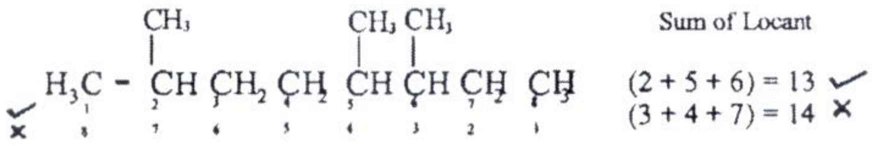
(II)

In structure (II), the straight chain contains only five carbon atoms whereas the longest continuous chain of carbon atoms contains eight carbon atoms and hence it is an octane chain. Straight chain is not the same as continuous chain so what is important is the longest continuous carbon atoms and not tie straightness or zig-zag nature of the chain.

It is possible that sometimes there may be two carbon chain having the same number of carbon atoms in the molecule. In such a case, the next rule will teach you how to select the longest continuous chain.

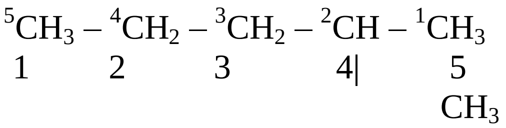
(ii) The second step is to number (Arabic numericals 1,2,3,, ..etc) the longest continuous chain from one end to the other in such a manner that the carbon atom carrying substituents get the lowest numbers.

The positions of the side chains or substituents are indicated by the numbers assigned to the carbon atoms to which they are attached. If there are more than one substituent then the numbering of carbon atoms is done in such a way that the sum of the numbers used to locate the subsituents is minimum. This is also known as the lowest sum rules. The number that locates the position of a substituent is known as Locant. (Structure III).



So Structure (III) is 2,5,6, trimethyloctane and not 3,4,7, trimethyloctane

(iii) The name of the substituents is prefixed, preceded by the Iticant, to the name of the parent chain A hyphen separates the 10Cfult from the name of the substituents e.g 2-methylpentane. (structure iv)

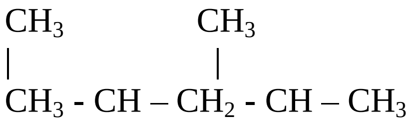


$$\begin{array}{ccccccccc} {}^{5}CH_3 & - & {}^{4}CH_2 & - & {}^{3}CH_2 & - & {}^{2}CH & - & {}^{1}CH_3 \\ 1 & & 2 & & 3 & & 4| & & 5 \\ & & & & & & & & CH_3 \end{array}$$

(iv)

- longest chain contains 5 carbon atom, so parent is pentane
- a -CH, (methyl) group located at 2 or 4; however is 2 smaller than 4, so 2-methylpentane

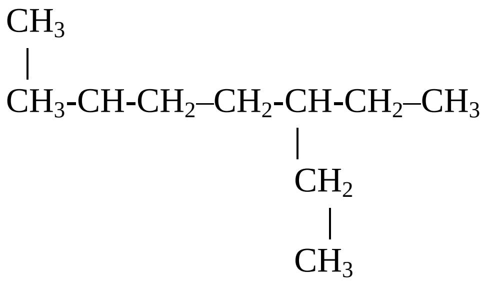
(iv) When there are more than one substitutent, each substituent is prefixed by its locant= and arranged in alphabetical order proceeding the name of the parents chain. The prefix di-, di- or tetra- (for two, three or four substituents), is attached to the substituatts name when more than one of a kind of substituans is present and the locants are written in increasing order separated by commas amongst themselves. (see Structure (III). However the prefixes di-, tri- or tam-, etc *are* not considered while deciding the alphabetical order of the substituents. Although this rule seems complicated the following examples will illustrate the rule and improve your understanding (Structure (v) — (vii)).



$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

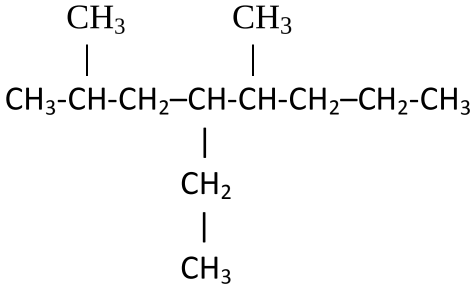
2,4-dimethylpontane

(v)



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

5-ethyl-2-methylheptane
(not 2-methyl-5-ethylheptane)
(VI)



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

4 - ethyl - 2,5 - ditnethylochme
(not 2,5 - rlimethyl - 4 - ethyloctane)
(VII)

- I am sure you feel a lot better now. Cart you then explain why the names in bracket for structures vi and vii are incorrect?

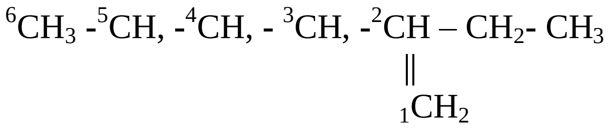
  Did your answer corresponds to this?

- For Structure VI, the name 2 methly-5- ethylheptane is incorrect because it violates the aliphabeti cal tide
- For structure VII, the name 2,3 ditnethy1-4-ethyloctane is incorrect because the prefix 'di-' was used in determination of the alphabetical order of substituents which should be based only of the names of the substituents - ethyl and dimethyl.

  Congratulations !!!

If however your explanation was wrong, use the explanation given to improve your understanding of the subject matter.

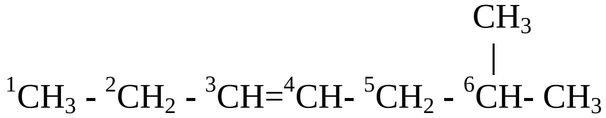
(v) When a double or triple bond is present in the molecule then the longest chain of carbon atoms is chosen as to include the multiple bond even if it is not longest continuous chain of carbon atoms. This rule is illustrated for you in structure VIII.



$$^{6}CH_3 - {}^{5}CH, - {}^{4}CH, - {}^{3}CH, - \underset{\underset{_{1}CH_2}{\|}}{{}^{2}CH} - CH_2 - CH_3$$

2 -ethyl- 1-h exen e (VIII)

Although the longest continuous chain is of 7 atoms but since it does not include the double bond, it is rejected as the parent chain and the carbon chain of 6 atoms (which is shorter) including the double is selected as the parent chain for naming the compound. The position of double or triple bond is indicated by prefixing the number of the carbon atom preceding the multiple bond.



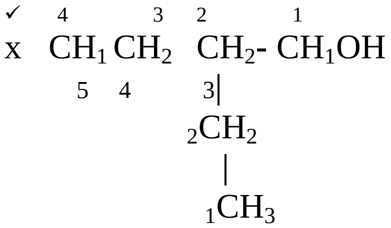
$$^{1}CH_3 - {}^{2}CH_2 - {}^{3}CH{=}{}^{4}CH - {}^{5}CH_2 - \overset{\overset{CH_3}{|}}{{}^{6}CH} - CH_3$$

(IX) = 6-methyl-3-heptene

The selected parent carbon chain is numbered in a manna that gives the lowest number to the multiple bond For example structure (IX) is named 6 - methyl-3-heptene and not 2-methyl-4-heptane.

3.1.3 Naming non-hydrocarbon compounds: Compounds with functional groups

You can still remember what functional groups are as learnt in unit 2.11 an organic compound contains a functional group, the longest carbon chain must be chosen as to include the functional group. The parent chain selected is numbered in a way to give the lowest number to the functional group even if it violates the lowest sum rule.



$$\begin{array}{lllll} \checkmark & 4 & 3 & 2 & 1 \\ x & CH_1 & CH_2 & CH_2- & CH_1OH \\ & 5 \quad 4 & & 3| & \\ & & & {}_{2}CH_2 & \\ & & & | & \\ & & & {}_{1}CH_3 & \end{array}$$

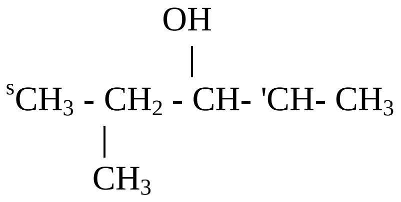
2-ethyl- 1-butanol

(C$_4$ not C$_5$ because only the C$_4$ contain the functional group)

The name of the substituents are prefixed to the parent hydrocarbon according to the IUPAC rules discussed in section 3.2.2, of this unit and the 'e' of the parent hydrocarbon name is replaced with the suffix of the functional group e.g.

- butane to butanol for alkanol
- hexane to hexacic acid for alkanoic acid
- butane to butanoate for alkanoate

This rule is illustrated in structures (X) and (XI) and will be applied in subsequent units this will improve your understanding of the concept.



$${}^{s}CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH_2}} - \overset{\displaystyle OH}{\overset{|}{CH}} - {'}CH - CH_3$$

$CH_3 - CH_2 - COOH$

3-methyl-2-perganol (X) propanoic acid (XI)

4.0 CONCLUSION

This is the end of the unit in which you have learned the basic IUPAC rules for naming organic compounds. The rules followed a systematic way of naming groups of compounds using the alkane *parent* compounds as the building block. The rules may appear difficult to apply at first but with practice you will get to understand it better and find it easy to use. Opportunity for more practice will be provided in subsequent units.

5.0 SUMMARY

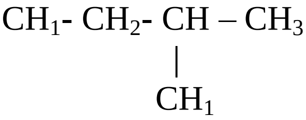
The I UPAC nomenclature for systemic naming of organic compounds involves the following rules.

- The longest continuous chain of carbon atoms containing the functional group is selected and named according to the parent alkane
- The selected parent chain is numbered to indicate the positions of any substituent in the chain and such numbering should give the lowest possible number to the carbon atom to which a substituent is attached.
- The name of substituents prefix the names of the parent alkane alphabetically and the positions of substituents preceed the names.
- The position of functional groups are given preference over those assigned to other substituents even lithe lowest sum rule is violated.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Give the I UPAC names of the following compounds

a)

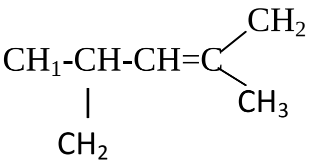


$CH_1\text{-}\ CH_2\text{-}\ \underset{\underset{CH_1}{|}}{CH} – CH_3$

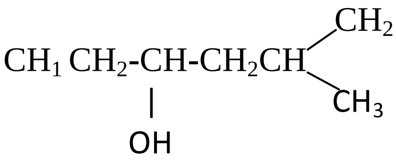
b)

$CH_2\text{-}\ CH = CH – CH_2\text{-}\ CH_3$

c)



(d)



ii. Draw the structures for the following IUPAC named compounds
   (a) 2 - ethylpentanol
   (b) 2, 3-dimethyl -2- octane
   (c) 3 -ethyl -2- methylheptane

7.0 REFERENCES/FURTHER READING

Norman R.O.C. and Waddington D. J. "Modern Organic Chemistry" Teweri IC S. Mehrotra V and Vishnoi, N. K. "Textbook of organic Chemistry".

UNIT 4 PURIFICATION METHODS AND THE DETERMINATION OF EMPIRICAL, MOLECULAR AND STRUCTURAL FORMULA ORGANIC COMPOUNDS

CONTENTS

1.0 INTRODUCTION

Organic compounds are usually represented in organic chemistry with formula, which is a shorthand method of showing the constituent atoms. The formula of a compound consist of chemical symbols of the constituent atoms and numerical subscript to indicate the ratio of the atoms. Recall that chemical bonds hold atoms together in the molecule and for organic compounds, the bond is essentially covalent. In the molecular orbital theory of covalent bonding, a bond is thought of in terms of the overlapping of two atomic orbitals each containing one electron. Covalent bonding formed by overlap of atomic orbitals are of two types, the sigma (α) bond and the pie (π)bond. All single bonds in organic compounds are of the α-type; double bonds consist of one α -bond and one to bond types; while triple bonds consist of one α bond and two π -bond types. Although when bonds between atoms are drawn, they are all represented with a straight line (-), it is important to note that these two types of bonds exist because they determine the reactivity of organic compounds.

Once an organic compound is prepared in the laboratory or isolated from some natural source, the procedure for the determination of its nature consists of the following steps.

i. state of purity and purification,
ii. determination of elemental composition-qualitative analysis,
iii. determination of relative numbers of each atom present in one molecule of the compound-quantitative analysis,
iv. determination of empirical and molecular formula,
v. determination of the structure of the molecule.

In this unit, our primary’ concerns are the methods for purification; determination of empirical, molecular and structural formula of organic compounds.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain the methods for the purification of organic compounds.
- derive the empirical and molecular formula of organic compounds
- draw the structural formula of organic compounds.

3.0 MAIN CONTENT

3.1 Purification Methods

Investigation of any compound must be preceded by careful purification to separate the pure substance from the impurities. In order to separate any two substances it is necessary to find some differences between them and the generally used ones are differences in solubility or vapour pressure (boiling point). The greater the differences between the two compounds the easier it is to separate them.

3.1.1 Distillation

This is a process used in separating two or more volatile, miscible liquids with different boilingpoints. For example a mixture of two liquids A (b.p. = 5($C) and B (b.p. 100°C). Distillation is of two types, simple distillation and fractional distillation. Simple distillation is used when the difference in boiling points, of the compounds to be separated is high; while fractional distillation is required when the boiling points are close and several compounds are to be separated.

The process of distillation involves boiling the mixture in a flask and the vapour from it is passed through a condenser. *Pure* liquid collects in a receiver and is referred to as the distillate; the impurities remain in the distillation flask. A simple arrangement is shown in Fig. 4.1

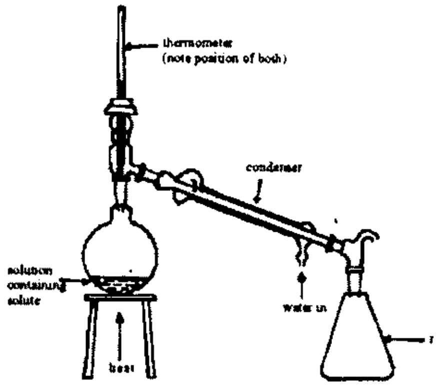


Fig 4.1 Simple distillation

The process of fractional distillation is not, however, always simple and straightforward as described 'above. It involves the *use* of fractionating column for good separation of liquids with very similar boiling points. Fractional distillation will be discussed in details in Unit 8 as it relates to the fractional distillation of crude oil or petroleum.

3.1.2 Crystallization

This is the commonest method for purifying a solid. The process of crystallization involves finding a solvent, by experimental trial, in which the solid is more soluble when the solvent is hot than when it is cold. The impure solid is then dissolved in the minimum amount of hot solvent, the aim is to get a solution which is nearly saturated at the boiling point of the solvent. The hot solution is then filtered, through a filter paper or funnel, so that any insoluble impurities can be removed. The filtration must be rapid to avoid crystallization during the process. A Buchner flask and funnel is the most suitable. (Fig. 4.2)

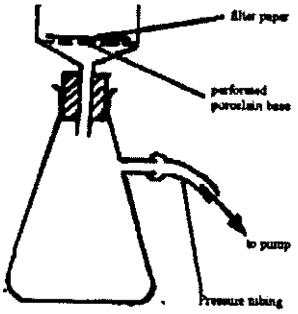


Fig. 4.2 Buchner *Flask* and Funnel

Soluble impurities remain, together with the solid required, in the filtrate. This is cooled for crystallization and the crystals formed are filtered off through a Buchner funnel. The crystals are then washed in the funnel with a little of the cold solvent and allowed to dry by pressing between filter papers or in a desiccator or oven.

Cryesiillisation is used in the nuutufacture of drugs and sugar.

3.1.3 Chromatography

Many natural products, for example extracts from plants and animals, are particularly difficult to purify. They may only be available in small quantities, they tend to decompose on heating, and the impurities *are* generally chemically similar to the product of interest Chromatography is a useful separation technique in situations where traditional methods of separation is not successful.

Chromatography involves moving a solvent over a porous, adsorbent medium (e.g. paper or powdered material such as silica and alumina) to separate a mixture of solute. There are many types of chromatographic techniques but our main concern in this unit is paper chromatography and column chromatography

(a) Paper chromatography

This uses one strip of chromatographic or filter paper as an adsorbent medium. A solution containing the mixture of solutes to be separated is spotted near one end of the paper. The paper is suspended in a closed air-tight jar with the spotted end (but not the spot) dipped into a suitable solvent e.g. hexane, water. *As* the Solvent front rises up the paper by ascending capillary action the various solutes present are carried forward at different speed. When the solvent front reaches almost to the top of the paper, the paper is removed and dried. If the solutes are coloured their positions on the paper can be seen. For colourless solutes the paper can be treated with appropriate chemical reagent to convert the solutes into coloured compounds. Each solute can then be identified by the distmce travelled and separated by cutting up each spot on the paper and each solute extracted separately. Fig. 4.3 shows a typical ascending paper chromatography set up.

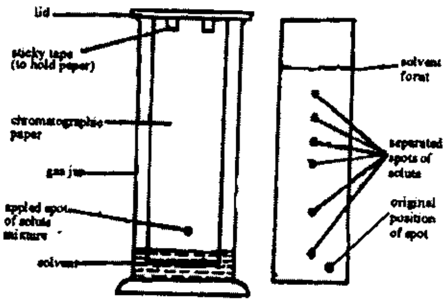


Fig. 4.3 Ascending paper chromatography

(b) Column chromatography

In column chromatography the solution containing the solutes is passed through a glass tube or column packed with solid adsorbent such as alumina or silica The mixture is then washed or moved through the column *using* an appropriate solvent. The solutes move through the column at different speed and are collected as separate component or fractions as the solvent elutes the column. The solvent is then evaporated to obtain each component of the mixture.

Many efferent packing materials e.g. alumina, silica, charcoal, starch, calcium carbonate, can be used. Typical solvents, which may be mixed together, include water, propanone, benzene, ethanol, trichloromethane and hexane. Chromatographic technique has been successfully used in the petroleum industry, hospital; food industry and research organization to effect the separation of mixtures of compounds.

3.2 Empirical and Molecular Formula

Qualitative and quantitative elemental analysis is used to know the various elements present and their relative composition respectively. Since a detailed study of these processes is beyond the scope of this programme, we shall discuss the next stage involved in the identification of an unknown organic compound, which is structural formula determination. The stages involve the determination oldie empirical formula and molecular formula of *the* compound fast; and then the structure, which shows the way the atoms are attached to one another, is then determined

3.2.1 Empirical formula

This provides information about the simplest ratio of the different atoms in a molecule eta compound, it does not give the actual number of atoms in the molecule. For example, the empirical formula of ethane, CH, CH, is CH_3 which is the same for all members of the alkane series (Unit 5). For ethanoic acid, CH_2CO_2H, the empirical formula is $CH_2$0 which is the same for glucose, cli$_n$k The empirical formula, therefore, gives the simple relative ratio of atoms of each element present in the molecule of the compound.

The basic steps involved in the determination of the empirical formula of an organic compound are:

(a) Write the percentage by mass of each element in the compound and the sum must add up to 100% (neglect experimental error). As a rule, if the sum is less than 100%, then the difference is allocated to oxygen atom.

(b) The percentage composition of each element is divided by the relative atomic *mass* of the elements in order to obtain the ratio of the moles of atoms present

(c) Then divide each ratio by the smallest ratio value to obtain the simplest whole number ratio (empirical ratio).

The following examples will help to illustrate these steps.

SELF-ASSESSMENT EXERCISE

Experimental determination of the elemental composition of an organic compound gave 79.9% carbon and 20.1% hydrogen by mass. Determine the empirical formula of the compound.

Solution 1

Since the percents" and H added up to 100%, then the compound contains C and H only.

Step I	Element	C	H
	%	79.9	20.1
Step 2:	%Ratio/Relative Atomic Mass	$^{799}/_{12}$	$^{20.1}/_{1}$
	Ratio of atoms	6.67	20.1
Step 3:	Smallest ratio	6.67/6.67	20.I/$_{6.62}$
	whole number ratio	1	3

Therefore empirical formula - C_1H_3 - CH_3

Example 2

An organic compound contains 26.7% carbon and 12% hydrogen. Derive the empirical formula of the compound

Solution 2

The % sum is 26.7 + 2.2 = 28.9% which is less than 100%; so the compound contains oxygen

Step1:	*Element*	*C*	*H*	*0*
	%	26.7	2.2	100- 28.9 - 71.1
Step 2:	% ratio/RAM	26.7/$_{12}$	12/$_{I}$	71.1/$_{16}$
	Ratio of atoms	2.22	2.2	4.44

Step 3: Smallest ratio $^{222}/_{2.2}$ $^{12}/_{2\,2}$ $^{4.44}/_{2\,2}$

1 1 2

The empirical formula C_1 H_1 0_2 = $CH0_2$

3.2.2 Molecular Formula

The molecular formula of a compound gives the exact number of moles of atoms of the component elements in one mole of the compound. In some compounds, the empirical formula and the molecular formula are the same. In other cases, the molecular formula is a simple multiple, n, of the empirical formula. For instance, ethanol, $C_2$1-1$_6$O has the same empirical formula and molecular formula; while both ethyne, C_2 H_2 and benzene, VI, have the same empirical formula, CH.

A simple relationship is: molecular formula = n x (empirical formula)

or $n = \frac{\text{molecular formula}}{\text{empirical formula}}$

(where n I, 2, 3, 4, 5 etc.)

To calculate the molecular formula of a compound It is necessary to experimentally determine the relative molecular mass of the compound. Details of the experimental procedure for molecular mass determination is beyond the scope of this programme. For gases and volatile liquids, once the relative vapour density is known, the relative molecular mass can be calculated using the relation

Relative molecular mass - 2 x Relative vapour density

The following examples will illustrate bow the molecular formula of compounds are estimated from empirical formula.

Example 3

The empirical formula for the compound in example 2 is $CH0_2$. Given that the relative molecular mass of the compound is 90, calculate its molecular formula.

Solution 3

Sum of relative atomic masses of the elements in the empirical formula

$CH0_2$= (12 x I)+ (1 x 1) + (16 x 2) = 45

$$n = \frac{molecular\ formula}{empirical\ formula} = \frac{90}{45}$$

n=2

∴ Molecular formula = 2 x (CHO_2) = $C_2H_20_4$.

Example 4

An organic compound with a vapour density of 45 was found to contain 54.5% carbon and 9.1% hydrogen. Calculate the molecular formula of the compound.

	C 54.5%	H 9.1%	0 100 - 63.6 - 36.4%
% / Ram	54.s/$_{12}$	9.1/$_{1}$	36.4/$_{16}$
	4.54	9,1	2.27
Dividing by smallest ratio	4.54/2.27	9.1/2.27	2.27/2.27
Whole member ratio	2	4	1
Empirical formula	C_211_40		

Relative molecular *mass*= 2 x vapour density

RAM -= 2 x 45 = 90

Empirical formula mass = (12 x 2) + (1 x 4) + (16 x 1) = 44

$$\therefore n = \frac{molecular\ formula}{empirical\ formula\ mass} = \frac{90}{44} = 2.05 = 2$$

Molecular formula r- 2 x (C_2H_40)=$C_4H_80_2$

3.3 Structural Formula

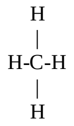
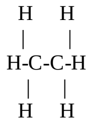
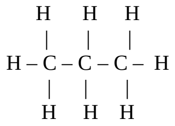
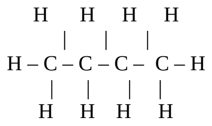
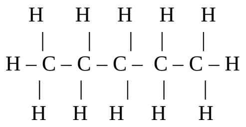
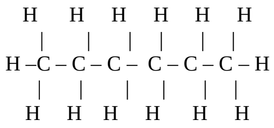
The structural formula of an organic compound gives information on the kind, number, arrangement and the nature of bonds of the atoms in the molecule. The structural formula therefore fully describes a compound The molecular formula as determined in section 4.3.2 does not have complete information about a compound, since it is possible for two or more compounds to have the same molecular formula but different structural formula --a phenomenon called isomerism (Unit 2).

The additional information required to move from molecular formula to structural formula of a compound can be obtained through:

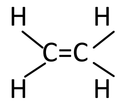
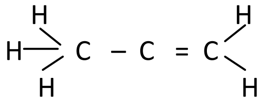
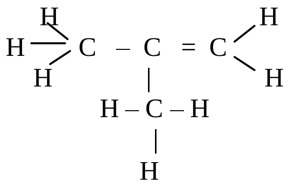
(a) physical properties determination e.g. colour, boiling point;
(b) the *use* of modem physical instrumentation *e.g.* mass spectroscopy, nuclear magnetic resonance, x-ray crystallography, etc. to establish structure.
(c) chemical reactions to determine the functionality (Unit 2) present in the structure.

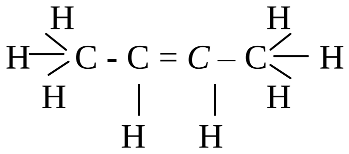
Once these information have been determined then the structural formula is drawn based on the information obtained and the molecular formula. Examples of the structural formula of several organic compounds based on their various functionality (Unit 2), are illustrated. You will learn more about the structure of these classes of compounds in subsequent units.

i) Alkanes

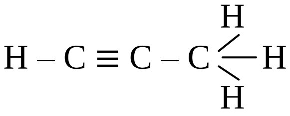
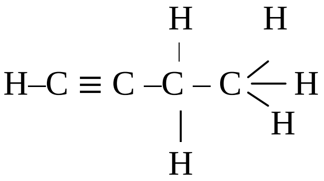
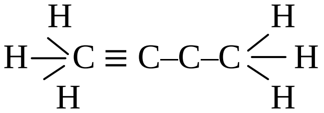
Name	**Molecular Formula**	**Structural Formula**	**Condensed Structural Formula**
Methane	CH_4	 $\begin{array}{ccc} & H & \\ & \mid & \\ H- & C & -H \\ & \mid & \\ & H & \end{array}$	CH_4
Ethane	C2He	 $\begin{array}{cccc} & H & H & \\ & \mid & \mid & \\ H- & C- & C & -H \\ & \mid & \mid & \\ & H & H & \end{array}$	H_3C-CH_3
Propane	C,H,	 $\begin{array}{ccccc} & H & H & H & \\ & \mid & \mid & \mid & \\ H- & C- & C- & C- & H \\ & \mid & \mid & \mid & \\ & H & H & H & \end{array}$	$H_3C-CH_2-CH_3$
Butane	C,H,,	 $\begin{array}{cccccc} & H & H & H & H & \\ & \mid & \mid & \mid & \mid & \\ H- & C- & C- & C- & C & -H \\ & \mid & \mid & \mid & \mid & \\ & H & H & H & H & \end{array}$	H_3C-CH_2-*CH_2- CH_3* or $H_iC(CH_2,CH_3$
Pentane	C,!ˉ!$_{12}$	 $\begin{array}{ccccccc} & H & H & H & H & H & \\ & \mid & \mid & \mid & \mid & \mid & \\ H- & C- & C- & C- & C- & C & -H \\ & \mid & \mid & \mid & \mid & \mid & \\ & H & H & H & H & H & \end{array}$	H,C CH,-C11,-C11,--CH, or H,C(CH,),CH,
Hexane	$C_6$1-1,,	 $\begin{array}{cccccccc} & H & H & H & H & H & H & \\ & \mid & \mid & \mid & \mid & \mid & \mid & \\ H- & C- & C- & C- & C- & C- & C & -H \\ & \mid & \mid & \mid & \mid & \mid & \mid & \\ & H & H & H & H & H & H & \end{array}$	1$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$ or H,C$(CH_2)_4$CH,

ii) Alkenes

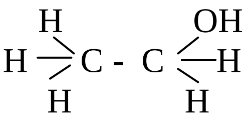
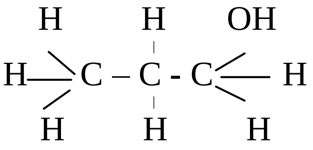
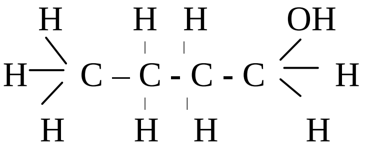
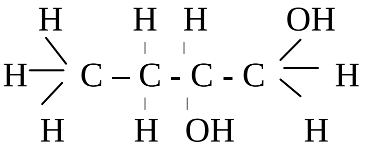
Name	**Molec**	**Structural Formula**	**Condensed**
Ethene	C_2E_4		$H_2C=CH_2$
Propene	C_3t1_6		$CH_3C11\text{-}CH_2$
2-nwthyl prop- I -ene	C,,H,		$(CH_3)_2$ C = CH_2

Name	*Molecular Formula*	*Structural Formula*	*Condensed Structural*
But-2-en	C4I-1,		CH_3 CH=$CHCH_3$

iii) Alkynes

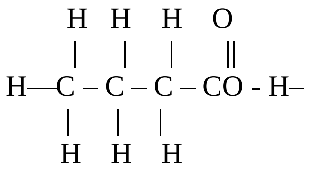
Name	*Molecular*	*, Structural Formula*	*Condensed Structural*
Ethyne	C_2H_2	H — C≡C—H	HC≡CH
Propyne	C_3H_4		HC≡ C-CH_3
I-Butyne	C_4H_6		HC ≡CCH_2CH_3
2-Butyne	C_4H_6		$H_3CC≡CCH_3$

iv) Alkanols

Name	*Molecular Formula*	*Structural Formula*	*Condensed Structural Formula*
Methanol	CH_40	H | H – C – OH |	CH_2OH
Ethanol	C_2H_60		H_3CCH_2OH
I -Propanol or Propan-l-ol	C_3H_80		$H_3CCH_2CH_2OH$
I –Butanol or Butan-l-ol	C_4 $H_{10}O$		$H_3C(CH_2)_2CH_2OH$
2-Butanol or Butan-2-ol	$C_4H_{10}O$		$H_3CCH_2CH(OH)CH_3$

v) Alkianoic Acids

Name	Molecular Formula	Structural Formula	Condensed Structural Formula
Methanoic acid	CH_20_2	0 || H—C - 0—H	HCOOH or HCO_2H
Ethanoic acid	$C_2H_4O_2$	H O | || H—C- C- O—H | H	CH_3COOH or CH_3CO_2H
Propanoic acid	C_3 H_6 O_2	H H O | | || H—C - C- C - 0—H | | H H	CH_3 CH2 COOH or $CH_3CH_2CO_2H$

Butanoic acid	$C_4H_8O_2$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}O-H-$	$CH_3CH_2CH_2C00H$ or $CH_3(CH_2)_2CO_2H$

4.0 CONCLUSION

In this unit you have learned about the methods for purification of organic compounds. You should also have learned about how to determine the empirical formula, molecular formula and structural formula of organic compounds. You should be aware of the stages involved and the calculation required to fully determine the chemical nature of organic molecules.

5.0 SUMMARY

What you have learned in this unit concerns distillation, crystallization and chromatography as purification methods in organic chemistry. In addition, you learned about method of estimating the molecular formula and hence structure of organic compounds. The unit that follows shall build up this foundation.

6.0 TUTOR-MARKED ASSIGNMENTS

i. (a) Describe, using adequate illustrations,
   (i) simple distillation
   (ii) paper chromatography
   (b) An organic compound contains 62.1% carbon and I 02% hydrogen by mass The vapour density of the compound is 29. Calculate its empirical and molecular fommla.
   (c) Write the structural formula of
   (i) But-I-ene
   (ii) propan-2-ol
   27

7.0 REFERENCES/FURTHER READING

Tewari, K. S., Mehrotra V. and Vishnoi, N.K. *'Textbook of Organic Chemistry'*.

UNIT 5 THE CHEMISTRY OF ALKANES

1.0 INTRODUCTION

In unit 3 you learned about hydrocarbons as organic compounds consisting of carbon and hydrogen only. You were also informed that hydrocarbons can simply be subdivided into alkanes, alkenes, alkynes and aromatic (specifically benzene) compounds. The nomenclature of these classes of hydrocarbon was also explained.

The alkanes, with a general formula CnH_{2n+2} or RH is the simplest homologous series and consist of saturated hydrocarbons. *Can* you recall the structures and names of the first ten members of the series'? Check your mac in unit 2 for a quick revision. The first three members of the series (methane, ethane and propane) only exist in the straight chain form but for the higher alkanes branched-chain isomers exist (refer to section on isomerism in Unit 2).

Alkalies, being saturated hydrocarbons are moderately inert and do not undergo any reaction other than combustion and substitution. They play an important part in petroleum chemistry (Unit 8). Alkanes are also referred to as paraffins from the Latin words meaning a little affinity. Because alkanes contain atoms which are linked by only single bonds (saturation), the few chemical reactions they undergo are mainly substitution type reactions-one atom being replaced by another.

2.0 OBJECTIVES

At the end of this unit you should be able to:

- recall the names and structures of the first ten members of the allcanes.
- list the natural sources and synthetic methods for alkalies.
- stale the types of reactions alkanes undergo in terms of starting material, reaction conditions and products
- enumerate the uses of alkanes

3.0 MAIN CONTENT

3.1 Natural Sources of Alka nes

3.1.1 Natural Gas

This is one of the major source of alkanes. Natural gas is found in the strata of the earth in different parts of the universe e.g. Nigeria, USA, Kuwait, Saudi Arabia, Iraq etc, and it is sometimes found associated with petroleum. Natural gas is the main source of methane together with smaller quantities of C_2 – C_6 alkanes (ethane, propane, butane, pentane anti hexane). The alkanes are separated by fractional distillation. If sulphur is present, it is oxidised to sulphur (VI) oxide, the precusor to H_2SO_4.

3.1.2 Petroleum or crude oil

Fractional distillation of petroleum provides a wide range of alkaves. The C_1—C_5 allcanes are also obtained like in natural gas and the fractious of higher boiling points contain mainly higher allcanes. Petroleum as a major source of alicanes will be discussed in more detail.

3.1.3 Vegetable Origin

Methane is obtained as product of anaerobic action on organic matter found buried in the earth or in sewages or in march gas and fire damp. Coal gas obtained from the destructive distillation of natural coal contains about 30% methane.

3.2 Laboratory Preparation of Alkanes

(a) Heating anhydrous salts of alicanoic (organic) acids. The $–CO_2$ - group of alkanoic acid can be removed by heating the sodium salts of the alkanoic acid with soda lime (a mixture of sodium and calcium hydroxides).

For example

$RCOONa' + NaOH \rightarrow RH + Na_2CO_3$
$CHCONa + NaOH \rightarrow CH_4 + NaCO_3$
Sodium (from soda methane
ethanoate lime)

The methane gas is collected over water.

(b) Wurtz coupling - alkyl halides e.g. iodoalkanes can be coupled in the presence of sodium metal to produce alkanes e.g.

$2RI + 2Na \rightarrow R\text{-}R + 2Nal$
$2CH,I + 2Na \rightarrow CH_1\text{-} CH_3 + 2Nal$
ethane

3.3 Properties of Alicitnes

3.3.1 Physical properties

(a) The boiling and melting points of simple gimes rise steadily as the number of carbon atoms increases due to the increasing strength of the van der waals'forces and increase in molecular mass. Thee is a gradation m state from gas to liquid to solid as you move from lower to higher members. e.g. methane, CH_4, is a gas, hexane $C_6\ H_{12}$ is a liquid dodecane $C_{12}H_{24}$ is a waxy solid.

(b) All alkanes are practically insoluble in water, and being less dense, the liquid and solid alkanes float on the surface of water. e.g. hexane, dodecane. That is why water cannot be used for putting out petrol and oil fires. The lower members of the alkane series are soluble in organic solvents.

3.3.2 Chemical Properties

(a) Combustion

Alicanes bum in an adequate supply of oxygen to form carbon (1V) oxide and water. This is also characteristic of other hydrocarbons - ethene, ethyne, benzene. In limited supply of oxygen, carbon (II) oxide and water is formed instead.

$CH_4 + 20_2 \rightarrow CO_2 + 2H_2O$
$2CH_4 + 3O2 \rightarrow 2C0 + 4H2O$ (limited supply of oxygen)
$2C_2H, + 70_2 \rightarrow 4CO_2 + 4CO_2 + 6H_20$

The ease of burning accounts for the use of many alkanes as fuels

.

(b) Substitution Reactions

One or more oldie hydrogen atoms in an allcane can be replaced by the halogens (CI, Br or I). The alkane reacts with chlorin; bromine or iodine in the presence of ultra-violet light or a temperature of about 400°C. The reaction is halogenation (addition of halogens) reaction and it is a substitution (replacing the hydrogen atom with another element) process.

$$CH_4 + Cl \xrightarrow[or\ 400^oC]{IV} CH_3\text{-}CI + HCI$$

$$CH \xrightarrow{CL} CH - CI \xrightarrow{CL} CHCI \xrightarrow{CL} CHCI \xrightarrow{CL} CCL\text{CH},$$

chloromethane dichloromethane trichioromethane telrachloromethane (carbon tetrachloride)

(c) Cracking

Is an important industrial process used for breaking large hydrocarbon molecules to smaller ones. Alkalies undergo industrially important elimination reactions in which they lose hydrogen. The reaction require a high temperature and, possibly, a catalyst. The products. are usually unsaturated hydrocarbons (alkenes and alkynes) and sometimes soot (carbon black) is formed.

$$C_2H_6 \xrightarrow{850^oC} H_2C = CH_2 + H_2$$

ethene

$$C_3H_8 \xrightarrow{Cr_2o_2Al_3o_3catalyst} H_2C\text{- } CH = CH_2 + H_2$$

propene

$$2C\ H_4 \xrightarrow{1500^oC} HC \equiv CH + 3H\ _2$$

3.4 Uses of Allkanes

(i) They are widely used as fuels - butane gas, petrol

(ii) Higher alkanes such as paraffin wax is used for candle manufacture, lubricants etc

(iii) Alkanes react with chlorine in the presence of light to give chloroalkanes e.g. chloroform, /KM in hospitals as an 'Anaesthetic', carbontetrachloride used as solvent for grease in dry cleaning and also in fire extinguishers.

4.0 CONCLUSION

You have learned the chemistry of the simplest homologous series consisting of the saturated hydrocarbon called alkanes. Alicanes constitute an important class of compounds because they are the major constituent of natural gas and petroleum which gives us our cooking gas, petrol, kerosene and several other useful products. With the study of the first homologous series of organic chemistry, you must begin to appreciate the relevance of organic compounds to us all.

5.0 SUMMARY

In this unit you have learned about alkanes as a class of saturated hydrocarbons. The primary sources of &lanes are crude oil and natural gas although they can be prepared on a small scale in the laboratory. Alkanes being saturated are moderately inert. However they undergo combustion, substitution and cracking reactions. Allcanes on their own are widely used as fuels and also in the manufacture of useful products like candles, lubricants and haloalkanes.

6.0 TUTOR-MARKED ASSIGNMENTS

i. List three natural sources of alkanes
ii. Use equations only to illustrate the combustion and substition reactions of a simple &Irene
iii. Enumerate four (4) uses of alkanes.

7.0 REFERENCES/FURTHER READING

Bah, ST., Tube, RD., Onwu, G and Obilcwere A. (2002) *Senior Secondary Chemistry Textbook 2* Lagos: Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry.* Onitsha: Africana-Fep Publishers.

MODULE 2

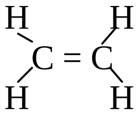
UNIT 1 THE CHEMISTRY OF ALKANES AND ALKYNES

CONTENTS

1.0 INTRODUCTION

You have learned in units 1 and 3 that hydrocarbons can be subdivided into saturated and unsaturated compounds. In unit 5 the learning centered on the saturated hydrocarbon called alkanes, which is the parent homologous series from which others are derived. In this unit the focus will be on the unsaturated hydrocarbons, alkenes and alkynes.

Alkenes and alkynes are classified as unsaturated hydrocarbons with general formula C_nH_{2n} and C_nH_{2n-2} respectively. They are characterised by the $C = C$ and C° C bonds respectively. Recall the systems of IUPAC nomenclature for these classes of homologous ending with the suffix -ene for a [Rene and --yne for alkynes.



H-C °C-H

ethene ethyne

Ethene and ethyne are the first members of the alkenes and alkynes series respectively.

You also learned in Unit 2, the concept of isomerism *and* that cis-trans isomerism exist in alkenes. Isomerism does not exist in allcynes because the molecules are collinear as learned in unit I The main feature of the chemistry of alkenes and alkynes is their addition reactions in which the C=C and C^O are converted into C-C bond For the alkenes, the products formed of such addition reactions with chlorine and bromine are oily liquids; hence the older name of 'olefines' for the series.

2.0 OBJECTIVES

At the end of this unit you should be able to:

- Identify the feature that differentiate unsaturated (alkalies) and unsaturated (alkenes and alkynes) hydrocarbons
- State the names and structures of all members of alkene and alkyne series up to $Cr_{10}H_{20}$ and $C_{10}H_{18}$ respectively.
- Discuss the sources and basic reactions of unsaturated hydrocarbons (alkenes and alkynes).
- Describe the laboratory method for detection of unsaluration.
- State why alkenes are important starting material for several industrial processes.

3.0 MAIN CONTENT

3.1 Sources of Alkenes and Alkynes

3.1.1 Natural sources of alkenes

(a) Cracking of alkanes

Natural gas contains large amounts of ethane, propane and butane; and these alkanes can be cracked either thermally or catalytically. The alkenes formed are then separated from the resulting gas mixture.

$$C_2H_6 \longrightarrow \underset{\text{ethene}}{C_2H_4} + H_2$$

$$\underset{\text{Propene}}{C_3H_6+H_2} \longrightarrow C_3H_8 \longrightarrow \underset{\text{ethane}}{C_2H_4 + CH_4}$$

(b) Cracking of naphtha

A mixture of naphtha and steam are heated to about 800°C. The cracked mixture obtained is then separated into a liquid fraction (provides fuel-oil and petrol) and a gas fraction which contains hydrogen, C_1-C_4 alkanes and C_1-C_4 alkanes. These gases can be separated by distillation under pressure.

3.1.2 Manufacture of ethyne

Ethyne is the most common member of the alkyne series and will therefore be used as the representative member for alkynes throughout this unit.

Modem processes produce ethyne, on a large scale, from methane or naphtha by applying a temperature of about 150ffiC for a fraction of a second. Hydrogen is obtained as a useful by-product.

$$2CH_4 \xrightarrow{1500^{0}C} C\ _2H_2 + 3H$$

This process has replaced the older method of obtaining ethyne by reaction between calcium dicarbide and water. The reaction still serves as a satisfactory source of ethyne on a small scale particularly for welding purposes.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2.$$

3.2 Laboratory Preparation of Ethene and Ethyhe

(a) Ethene by dehydration of Ethanol

Etliene is produced by dehydration (removal of water) of ethanol. This can be achieved in two ways, either by passing the vapour of ethamoi over finely divided aluminium oxide heated to 308C; or heating the ethanol with excess concentrated tetraoxosulphate (vi) acid at 180'C. Both reagents act as dehydrating agents.

$$C_2H_4 + H_20 \xrightarrow[300^{0}C]{A1_3O_3} \underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[300^{0}C]{\text{excess co if so}} C_2H_4 + H_20$$

b) Ethyne from calcium dicarbide

The reaction of calcium dicarbide with water, as discussed in section 6.2.2 of this unit, is the method used to obtain ethyne in laboratory.

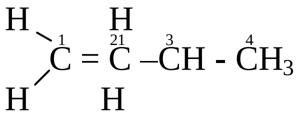
3.3 Isomerism in Alkenes

You will recall that in Unit 2, the concept of isomerism was discussed and alkenes are said to exhibit cis-trans isomerism. All akenes above C_3H_6 show isomerism. For C_4H_8, recall the structure of cis-but-2-ene and trans-but-2-ene.

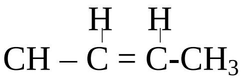
SELF-ASSESSMENT EXERCISE

Can you explain why I- butene does not exhibit cis-trans isomerism?

Apart from cis-trans isomerism, alkenes also show a type of structural isortterism known as positional isomerism. This type of isomerism is dependent on the position of the double bond as well as the way atoms are arranged in the molecule, For C_4H_8, three structural isomers arc known.

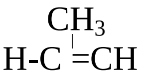


but - I- ene



$CH - \overset{H}{C} = \overset{H}{C}-CH_3$

but -2- cne



$H-\overset{CH_3}{C} =CH$

2-rnethylpropene

3.4 Chemical Properties

3.4.1 Alkenes

(a) Addition reactions

Alkenes are unsaturated due to the presence of C - C and therefore atoms can add across the double bond to give addition products and in the process convert C = C to C - C bond. Four types of molecules, H, halogens ($C1_2$, Br_2, 1_2), hydrogen halides (HCI, HBr_2, HI) and H_20; can add on to the C = C.

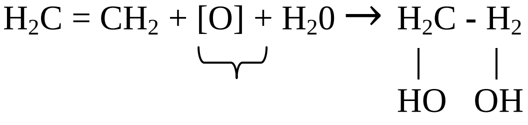
- $H_2C =CH_2 + H_2 \xrightarrow[2000C]{\text{Ni or Pi}} H_3C - CH_3$ hydrogenation (useful for the hardening of oil to margarine)
- $H_2C = CH_2 + CI_2 \xrightarrow[\text{room}]{\text{tempo}} CICH_2 - CH_2CI$ halogenation (e.g chlorination)

- $H_2C = CH_2 + HI \xrightarrow[\text{room}]{\text{tempo}} H_3C\text{-} CH_21$ Hydrohalogenation (e.g hydroiodination)

- $H_2C = CH_2 + H_20 \xrightarrow[80^{O}C]{H_2SO} H_3C - CH_2OH$ Hydration

(b) Oxidation reaction

Aqueous solution of potassium tetraoxomaganate (VII) acting as an oxidizing agent can add two -OH groups onto C = C of alkenes.



$$H_2C = CH_2 + \underbrace{[O] + H_20}_{} \rightarrow \underset{HO}{\underset{|}{H_2C}} - \underset{OH}{\underset{|}{H_2}}$$

from
KMnO$_4$ Solution

Ethane-1, 2-dial
(Ethylene glycol)

(c) Polymerisation Reaction

This F. an industrially important reaction of alkenes. Polymerisation is the process by which many simple molecules (called monomers) join together to form very giant molecules (called polymers), Alkenes, particularly ethene, is an important monomer and undergo addition polymerisation. For ethene.

$2nCH_2 = CH_2 \rightarrow \ldots(\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-})\text{-}_n$

ethene Poly (ethenc)
(Polythene)

Polythene is widely used for making buckets, pipes, bottles, cups, spoons, toys, packing materials and cable insulating materials.

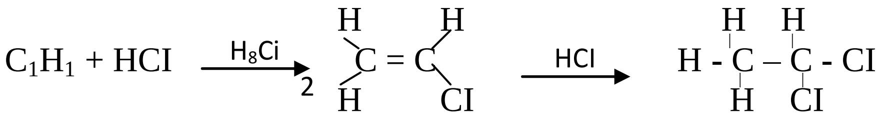
3.4.2 Alkynes

(a) Addition Reactions

Alkynes, like alkenes, are unsaturated and so undergo addition reaction. For alkynes the reaction occurs in two stages, the first addition converts the C° C to C = C and the second addition converts C = C to C - C. For example:

$$HC^{O}\,CH \xrightarrow[150^{O}C]{H_2/Ni} H_2C = CH_2 \xrightarrow[150^{O}C]{H_2/Ni} H_3C\text{-}CH_3$$

$$C_2H_2 + 2CI_2 \xrightarrow{FeCl_1} C1_2CH - CHCI_2$$



Chloro ethene
(vinyl chloride)

1,1-dichloroethane

The chloroethene product is important in making polyvinyl chloride (PVC), an inert polymer used as insulating materials for electrical cables, boots.

b) Polymerisation

Ethyne does not polymerise so really as ethene. On heating, however, ethyne is polymerised to benzene, and important hydrocarbon that will be studied in Unit 7.

3.5 Test for Unsaturation

The presence of multiple bonds (unsaturation) as found in alkenes and alkynes can be detected in the laboratory using two common reaction studies in Section 6.5

(a) Bromine in carbon tetrachloride (Br_2/ CCl)

When an alkene or alicyne is passed through Br_2/CCI_4 or bromine water (brown) there is decolourisation because the bromine which is responsible for the brown colour adds across the multiple bond.

(b) *Aqueous potassium permanganate [$KMn0_4(aq)$]*

The purple colour of $KMnO_4$(aq) disappears (decolorised) when any unsaturated hydrocarbon (alkenes and alkynes) is passed through. This is an oxidation process in which the purple Mn(VII) is converted to colourless Mn(V).

The two tests are used to distinguish saturated alkanes from unsaturated alkenes and alkynes.

4.0 CONCLUSION

You have learned the chemistry of the aliphatic unsaturated hydrocarbons, alkenes and alkynes. The principal source of alkenes and alkynes is from the parents hydrocarbon, alkanes, obtained from natural gas and petroleum. However, the reactivity of alkenes and alkynes are different from those of alkanes because of the presence of multiple bonds. Their reactions are essentially addition to the multiple bonds hence they are far more reactive than alkanes. Several of these reactions are industrial processes that lead to useful end products.

5.0 SUMMARY

What you have learned in this unit is about unsaturated hydrocarbons - alkenes and alkynes. Their chemistry is essentially centered on the multiple bond which are convened to saturated bonds by several reagents like hydrogen, halogens, hydrogen halides and water. In addition, alkenes undergo polymerization reaction to give useful polymer materials.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Drmwthe structure and name all the two geometric and five structural isomers of
ii. Explain, with varied illustrative examples, the meaning of the term addition reaction.

7.0 REFERENCES/FURTHER READING

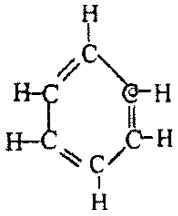
Osei Yaw Ababio *(2002) New School Chemistry.* Onitsha. Africana-FEP Publishers.

UNIT 2 INTRODUCTION TO THE CHEMISTRY OF BENZENE

CONTENTS

1.0 INTRODUCTION

In units 5 and 6 you learned about the aliphatic hydrocathons-alkanes, aficenes and alkynes as distinct homologous series. There are a number of homologous series of aromatic hydrocarbons or arenes. The simplest, based on benzene, C_6H_6 and containing one ring of six carbon atoms have a general formula C_nH_{2n-6}, $(n \geq 6)$. The chemistry of benzene, the simplest aromatic hydrocarbon, is the subject of this unit. Aromatic compounds were originally so named because many of them were fragrants and the term aromatic is derived from the Greek word aroma, meaning pleasant smell. The structure of benzene is represented simply as a conjugated (alternating single and double bonds) system of three double bonds forming an hexagonal ring with the carbon atoms.



The benzene ring as represented above is not strictly on alternating single and double bonds in cyclic form but an acceptable and convenient way of drawing the structure of benzene. The true nature of the bonds is explained in this unit.

Other members of the benzene homologous series are formed by successive replacement of hydrogen atoms by-CH_3 groups. Only benzene, as representative of the series, will be discussed in this unit as the chemistry of the other members are beyond the scope of this programme.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain the concept of resonance in terms of delocalisation of electrons.
- explain the unusual stability of the benzene nucleus in terms of resonance.
- compare the reactions of benzene with those of the other unsaturated hydrocarbons, (alkenes and alicrtes).
- discuss the types of reactions benzene undergo.

3.0 MAIN CONTENT

3.1 Structure and Bonding in Benzene

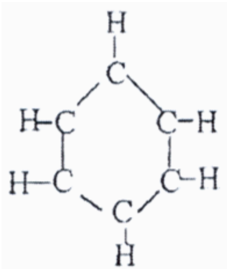
Benzene is normally drawn as a six-membered carbocychc ring with alternating single and double carbon-to-carbon bonds. Each carbon is connected to a single hydrogen. Is benzene simply a cyclic alkene? On the account of the structure, the C=C should behave like those found in alkenes, but benzene does not behave like alkenes i.e. it does *not* give addition products across the C=C like alkenes.

Studies have shown that benzene is a regular planar hexagon, with the carbon-carbon bond length of 1.39run. This bond length is shorter than the C-C bond length of alkanes (1.540m) and longer than CC of alkanes (1.34nm). For *benzene*, however, the carbon-to-carbon bonds for all the six carbon atoms in the ring is I .39nm; an intermediate value between the single and double carbon-to-carbon bond. How can this observation be explained? The solution lies in the concept of a phenomenon known as resonance.

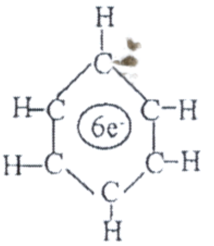
3.1.1 Resonance in Benzene

To explain the unusual observation in respect of the benzene structure, we have to recall that we have discussed bonding only in terms of electron pairs associated with two nuclei. These we may call localised electron i.e. shared bonding electrons located between the two bonded atoms. The fact, however, is that bonding electrons can be associated with more than two nuclei, and there is a measure of stability to be gained by this because the degree of bonding increases when the electrons can distribute themselves over a greater volume. This effect is called electron delocalization or resonance.

Let us now see how this concept can be used to explain the benzene ring structure i.e. all the carbon-to-carbon bonds in the ring are usual. You will recall (unit I) that carbon has four electrons available for bonding. Let us lock at a typical six carbon ring system similar to



that proposed for benzene but with only the single bonds shown Focus your attention on the asterisk carbon atom. It has four valence electrons, one is used for bonding with hydrogen atom and one used each to bond with one carbon to the right and one to the left, making a total of three electrons used for bonding and one electron unused. This statement is true for all the six carbon atoms in the ring, giving a total of six unused electrons. Rather than localising any of these six electrons, as pairs of electrons between two adjacent carbon atoms, to form three bonds usually shown as the three double bonds (π bonds) in the benzene; the six electrons are delocalised (resonance) between all six carbon atoms. In other words, the six unused electrons are pooled together as electron cluster from which any of the six carbon atoms can pool from. Study the representation below



The structure above gives a better picture of the benzene molecule although the earlier shown in the introduction is still acceptable once it is clear that the bonds are not actually alternating single and double bonds. The true structure of &Irene is a resonating hybrid of various resonance structure in which there is movement of electrons; most of the time delocalised but sometimes localised in a dynamic equilibrium

$$\begin{bmatrix} The \leftrightarrow is\ used\ as\ symbol\ to \\ represent\ resonance \end{bmatrix}$$

This suggestion is in agreement with the fact that all the carbon-to-carbon bonds in benzene are of the sane length, and intermediate between the C-C single bond of alkanes and the C=C double bond of alkenes. This concept of resonance confer stability on the benzene, hence any attempt to change (e .g addition reaction), this arrangement

can lead to instability; and it is normally' resisted.
It is the lack of simple C-C and C=C bonds which make the properties of benzene different from those of the domes and alkenes, and the delocalisation in the benzene molecule is the cause of aromatic character. Therefore, benzene though unsaturated like alkenes and alkyl:es 'does not decolourise bromine water and aqueous potassium tetraoxomanganate since it does not undergo substitution reaction.

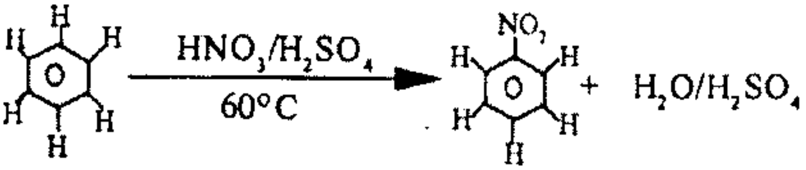
3.2 Chemical Properties of Benzene

The stability of the aromatic nucleus in benzene due to resonance means that it does.not undergo similar reactions like alkenes; even though it is also unsaturated. Benzene reacts mainly by substitution in which the hydrogen atoms are replaced with other groups while still retaining its aromatic stabilization. In sane reactions, however, this aromatic stabilization is lost and benzene undergoes addition reactions such as catalytic hydrogenation.

3.2.1 Substitution Reactions of Benzene

(a) Nitration

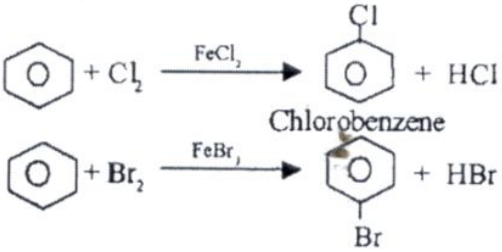
A mixture of concentrated trioxonitrate (V) HNO, and tetraoxosulphate (VI), H_2SO_4; acids reacts with benzene, at 60°C, to form nitrobenzene



Nitrobenzene

(b) Halogenation

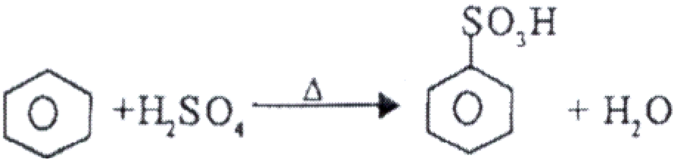
Benzene reacts with chlorine or bromine in the presence of a reagent called Lewis acid ($FeCl_3$ or $FeBr_3$) to form chloro-or bromo-benzene. Light must be excluded from the reaction mixture.



Bromobenzene

(e) Sulphonation

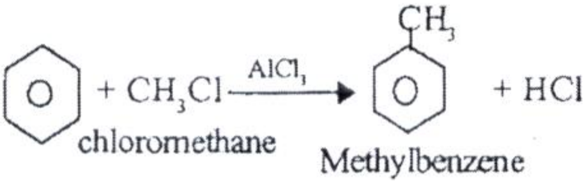
Benzene reacts on heating with concentrated tetraoxosulphate (VI) acid, H_2SO_4, to form, benzenesulphonic acid.



Benzasulphonic acid

(d) Alkylation

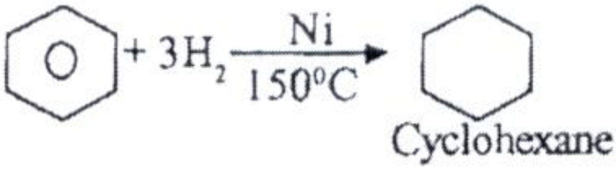
Benzene and halogenoalltanes e.g. chloromethane react, in the presence of Lewis acids, $AlC1_3$, as catalyst, to form alkyl benzenes e.g. methylbenzene. The reaction is known as the Friedel-Crafts reaction,



3.2.2 Addition Reactions of Benzene

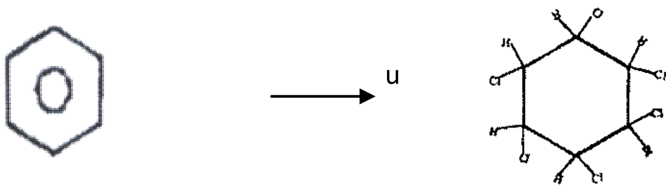
(a) Hydrogenation

If a mixture of hydrogen gas and benzene vapour is passed over finely-divided nickel at 150°C, the benzene is reduced to cyclohexane.



(a) Halogenation

Chlorine and bromine add on to benzene in the presence of sunlight or ultra-violet light producing, for example 1,2,3,4,5,6, -hexachlorocyclohexane



hexachlorocyclohexane

4.0 CONCLUSION

You have been introduced to the chemistry of benzene, the simplest of the aromatic hydrocarbon series. You should have also realised the importance of resonance in the understanding of the study of aromatic compounds in general *and* specifically benzene. The effect of aromatic stabilisation is that aromatic compounds e.g. benzene do not react like alkenes despite the fact that they are also unsaturated.

5.0 SUMMARY

- In this unit, you were introduced to benzene as an unusually stable unsaturated hydrocarbon. The nature of the structure and bonding in benzene was explained using the resonance concept.
- The reactivity of benzene towards organic reagents shows that it reacts mainly by substitution reactions as opposed to addition reactions observed with the unsaturated hydrocarbon, alkenes. This shows that the bonds in benzene are different from those of alkenes.

6.0 TUTOR-MARKED ASSIGNMENTS

Use the *e ,ncept* of resonance to account for the structure of benzene. (10) Use equadons only to illustrate four substitution reactions of benzene.

7.0 REFERENCES/FURTHER READING

Bajah, S. T., Teibo, B. 0., Onwu, G. and Obilcwere, A. *(2002)Senior Secondary Chemistry* - *Text book 2.* Lagos. Longman Publishers.

Holtzclaw, A. and Robinson, W. It General Chemistry.

UNIT 3 INTRODUCTION TO PETROLEUM CHEMISTRY

CONTENTS

1.0 INTRODUCTION

Petroleum also known as crude oil is a viscous liquid mixture of organic compounds deposited in the strata of the earth. Crude oil is found in Nigeria, U.S.A., Kuwait, Saudi Arabia, Iraq, etc. It varies widely in composition but consists mainly of alkanes (C_1 to C_{40} per molecule), cycloalkanes and aromatic hydrocarbons It may also contain some proportions of sulphur, nitrogen, oxygen, etc.

Crude oil is believed to have been formed by the bacterial decomposition, under pressure, of animal and plant remains. Petroleum is an extremely important raw material. It is required both to provide fuels for energy generation and as source of many organic and inorganic chemicals.

Petroleum is extracted from the earth crust essentially through drilling. This is then followed by a difficult process of separating the individual component through the refining process. The process of petroleum refining is basically that of converting crude oil into a range of high quality economically important products.

The complex mixtures of hydrocarbons present in the crude exist in gaseous, liquid or solid forms Also present with the crude are a number of 'inorganic impurities' that are detrimental (dangerous) to the refining process; and solid impurities such as sand. Petroleum is sometimes found associated with 'Natural Gas'.

2.0 OBJECTIVES

At the end of this unit you should be able to:

- describe the fractional distillation of petroleum process.
- list the essential fractions obtained from the distillation process.
- define the term cracking and reforming; and their relevance in the petroleum industry.
- list the uses of the factions of the refining process.
- explain the importance of octane wither in petrol quality.
- discuss how petroleum has affected the economy of Nigeria.

3.0 MAIN CONTENT

3.1 Crude Oil Reserves

About 60% of the world's oil reserves are found in Asia, with the Middle East (Saudi Arabia, Iraq, Iran, Kuwait, Bahrain, Oman) having the lion share. China and Indonesia are other Asian countries with large oil reserves. Russia as a country has the largest reserve in the world. Large deposits of crude oil is also found in United States, Venezuala, Canada, Australia and in some West African countries e.g. Nigeria.

The Nigerian crude oil reserve was discovered in 1956 at Oloibiri. Since then crude oil has become the principal source of revenue for Nigeria. Large deposits of crude oil has been found in the Niger Delta region - Afam, Abata, Bomu, Owaza, Egbema, and the Ughelli-Kokori - Oleh zone. Offshore, crude oil has been found around Calabar and in the Burutu - Forcados - Escravas zone of Delta State. From all these oil fields, the crude is pumped through pipes to the oil terminals at Bonny or Forcados for export or to our refineries located at Want Port-Harcourt and Kaduna.

3.2 The Refining Process

There are two main stages, desalting and distillation processes. The desalting is simply a process of removing salt compounds; and is more of a mechanical process than chemical which is beyond the scope of this programme.

3.1.1 Fractional Distillation

This process facilitates the separation of the petroleum into 'fractions' or 'cuts' hence the name fractional distillation, which is the principal method for the purification of petroleum. Crude oil is heated to about 400°C by passing it through coils of pipes in a gas-heated pipe-still furnace.

The resulting hot oil, which is at 400°C is a mixture of vapours and liquids, is passed into a tall cylinder known as a fractionating tower or column, The column is divided into a number of compartments by means of trays, which contain holes covered by 'bubble-cap' and overflow pipes.

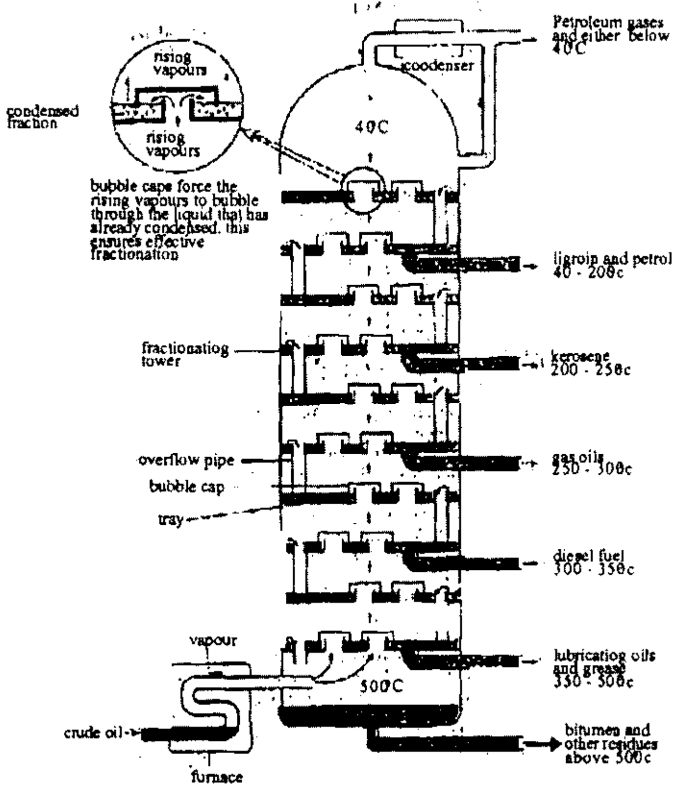


Fig 8.1: Fractionating column for fractional distillation of crude oil

The temperature of the fractionating column ranges from about 400°C at the bottom to about 40°C at the top, and each tray is at a controlled temperature. As the mixture passes into the column, the liquids fall to the bottom whilst the vapours pass up through the trays. As each tray is at a different temperature, different mixtures of vapour condense to give different petroleum fractions in each tray.

The main fractions collected and their uses are tabulated in Table 8.1

Fraction	Roiling Range ^{o}C	Approximate	Use
Gas fraction	< 40	1-5	gaseous fuel for cooking and heating; source of alkanes
Petroleum ether	40-66 60-80		solvent
Petrol or gasoline	70-180	5-10	fuel
Naphtha	100-200		solvent; source of alkanes and alkenes
Kerosine or Paraffin oil	200-300	11-14	Fuel oil lanterns, tractor and jet engines
Light gas-oil or fuel oil	250-400	13-17	Fuel oil for diesel engines
Heavy gas oil, light lubricating oil	300-400	18-25	Fuel, lubricants, paraffin wax, medicinal paraffin.
Residue	> 400	> 25	Bitumen for surfacing road and roofing materials.

Nigeria has three refineries located at Kaduna, Port-Harchourt and Want They refine the crude oil to meet the domestic needs of petroleum products, e.g. petrol, kerosene, diesel, butane gas etc., and some of the products are exported to neighouring countries e.g. Niger, Chad.

3.1.2 Quality of Petrol - Octane Number

Most of the gasoline fraction obtained from the column, requires further treatment as it knocks easily if used directly. This means that the petrol-air mixture in the cylinders, when it is being used as fuel in engines, explodes prematurely and incompletely causing a metallic rattle known as knocking.

The knock properties of a petrol is measured by its octane number, 2, 2, 4-Trimethylpentane (iso-octane) cause almost no knocking (octane number 100) and heptane, which knocks very readily (octane number 0), have been chosen as standards against which the performance of any petrol can be measured. The octane number of any fuel is the percentage of iso-octane in a mixture of iso-octane and hermitic that will knock to the same extent as the fuel under the same conditions. The difference in the grades of petrol is the difference in their octane number.

The octane rating of a fuel can be improved by adding anti-knock agents such *as* tetraethyl lead. Also, straight-chain alkanes (e.g. heptane) cause knocking far more readily than branched-chain alkanes (e.g. isooctane). Alkenes and aromatic hydrocarbons have better known qualities than straight-chain alkanes. So delicate conversion processes has been developed that balances all these characteristics to change the composition of the original gasoline fraction.

SELF-ASSESSMENT EXERCISE

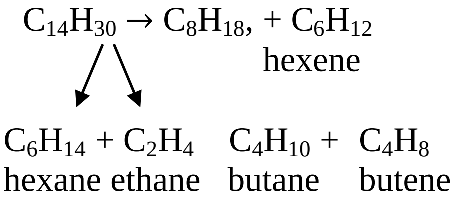
Draw the structural formula of iso-octane and heptane.

3.2 The Conversion Processes

The distillation process merely separates the crude oil into various fractions but it cannot change the proportion of the constituent hydrocarbons in the fractions. These proportions vary with the source of crude oil and in most cases do not meet the standard for their desired use. Both the yield and quality of the fractions can be improved upon by various convers^1 on processes.

3.2.1 Cracking

In the cracking process larger hydrocarbons in fuel oil fractions are broken down into smaller hydrocarbons needed in petrol. This same process also converts some of the straight-chain alkalies (which knock easily) into branched-chain alkanes. Cracking can be achieved at high temperature and pressure (thermal) but cracking using catalyst is more common. Alkanes (saturated) with lower relative molecular mass are produced, together with a mixture of gaseous alkenes e.g., C_2H_4,C_3H_6, C_4H_8.



$$C_{14}H_{30} \rightarrow C_8H_{18}, + C_6H_{12}$$

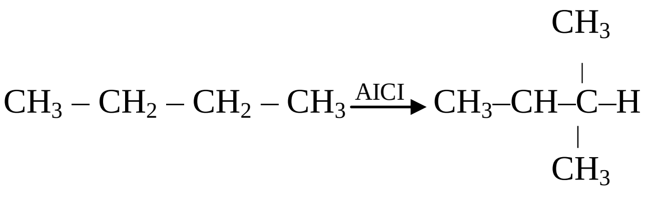
hexene

$$C_6H_{14} + C_2H_4 \quad C_4H_{10} + C_4H_8$$

hexane ethane butane butene

3.2.2 Isomerisation

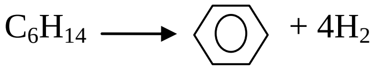
In this process, straight-chain alkanes are converted into branched-chain isomers at about 100° C and under pressure; with $AlC1_3$ as catalyst



$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{AICI} CH_3\text{–}CH\text{–}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{–}H$$

3.2.3 Reforming

This process involves the conversion of straight-chain alkanes into aromatic hydrocarbon. The process involves a simultaneous cyclisation (forming ring compound), catalyst by $A1_20_3$; and dehydrogenation, catalyst by platinum.



In these conversion processes, more useful alkanes and alkenes are produced and straight-chain alkanes are transformed to branched alkanes and aromatic hydrocarbon; all of which improves the octane number or quality of petrol.

3.3 Petrochernicals

The term petrochemicals is used to describe the chemicals obtained from petroleum which are useful raw materials for the chemical industries.

The gas and naphtha fractions from the fractional distillation of petroleum, together with gases obtained from cracking process, and natural gas, provide the major starting materials. They serve as a source of these petrochemicals - methane, ethane, propane, butane, ethene, propene, butenes and aromatic hydrocarbons such as benzene, toluene and xylenes; which are starting materials for a very wide range of important products, e.g plastics, cosmetics, pharmaceutics, detergents and synthetic fibres such as nylon. The petrochemicals are often referred to as value-added products.

There are three petrochemical factories in Nigeria located in Lagos, Port Harcourt and Kaduna. When fully functional, they will produce important petrochemicals such as synthesis gas, alkenes and aromatic compounds. From the synthesis gas, we can produce ammonia, methanol, gasoline, fertilizers, refrigerant, explosives, urea, polymers, etc. From the alkenes, we can produce several types of polymers eg. polythene, nylon; ethanol, cosmetics, synthetic rubber. From the aromatic compounds we can produce insecticides, detergents, solvents, nylon. These products will increase our export earnings and reduce our dependence on importation of finished products.

3.4 Oil Production and the Nigerian Economy and Environment

The production of oil in Nigeria has increased steadily since 1956, when oil *was* first discovered. Nigeria now ranks among the top ten oil producers in the world. By 1975, petroleum accounted for about 90^0/o of all export earning of Nigeria and is still the major source of foreign exchange earnings. The earnings form petroleum exports have been used for development projects in agriculture and industry, as well as to construct many roads, buildings and set up several public utilities services.

The extraction, transport and refining of crude oil has provided employment opportunities for Nigerians the proposed petrochemical industry become fully functional, Nigeria's earnings will increase and more jobs will be provided. Petroleum products such as plastics, detergents, insecticides, etc have become part of our lives and has greatly improved our standard of living.

The availability of petrol has lead to a tremendous increase in the number of motor vehicles on roads of Nigerian cities. The distribution of population within the country has changed since the discovery of petroleum because of job-related mobilities and the need for better living.

The benefits of petroleum are enormous however it also brought along some serious environmental pollution problems. The emissions of pollutants such as hydrocarbon gases, tetraethyl lead, carbon (II) oxide, nitrogen oxides, sulphur (IV) oxides etc. have made our environment less safe. Besides air pollution, there is also the problem of oil spills which destroy marine life.

4.0 CONCLUSION

In this unit you have been introduced to the chemistry of petroleum, which is an extremely important raw material. Although the composition of petroleum vary with source, the principal component still remarried alkalies which are separated into various fractions by fractional distillation. The end products of this process have varied applications in the world and no fraction is useless. More useful fractions can be obtained from the less useful ones by various conversion processes. Some products of the conversion process are useful petrochemicals which are important starting materials for the chemical industry.

5.0 SUMMARY

In this unit, you learned about the source and composition of crude oil. Crude oil as obtained from the earth crust is converted to more useful products through the refining process, principal of which is fractional distillation.

Fractional distillation separates petroleum into fractions based on boiling ranges and these fractions are used mainly as fuels. Several conversion processes are known which improves the quality of the fractions e.g. petrol and provide useful petrochemicals for the chemical industries.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Describe the fractional distillation of petroleum and list the fractions obtained with their uses.
ii. Explain the tam octane number and its importance in determining the quality of petrol.
iii. Describe cracking and reforming as conversion processes in the petroleum industry.

7.0 REFERENCES/FURTHER READING

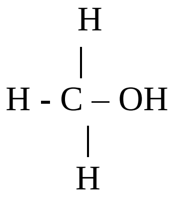
S.T., Teibo, B.O., Onwu, G. and Obikwere, A. *(2002) Secondary Secondary Chemistry Textbook I.* Lagos. Longman Publishers.

UNIT 4 ALKANOLS I USES ALKANOLS

CONTENTS

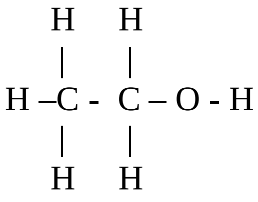
1.0 INTRODUCTION

In unit 2 you learned about organic functional groups. Allcanol are a group of compounds in which the hydrogen atom(s) of allcanes have been replaced with the hydroxyl (-OH) functional group. Alkanols are generally referred to as 'alcohols'. You will also recall that the general formula of alkanols is C_nH_{2n+1} OH and are named by replacing the `e' of the alkane name by 'ol.' For example methanol and ethanol from methane and ethane.



$$H - \underset{H}{\overset{H}{C}} - OH$$

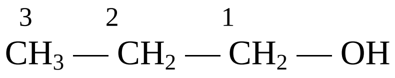
methanol



$$H - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - O - H$$

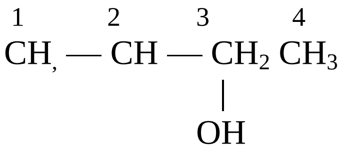
ethanol

A simple general representation for allcanols is R-OH, where `R.' represents an alkyl group. When necessary, the position of the -OH group is shown numerically, e.g propanol. The carbon atoms are numbered in the longest chain. The position of the OH group determines the numbers. Study the structures below.



$$\overset{3}{CH_3} — \overset{2}{CH_2} — \overset{1}{CH_2} — OH$$

propan- I-ol or 1-propanol



$$\overset{1}{CH_{,}} — \overset{2}{CH} — \underset{OH}{\overset{3}{CH_2}}\ \overset{4}{CH_3}$$

propan-2-ol or 2-propanol

This is postional isomerism, a form of structural isomerism which you learned in units 2 and 6.

The hydroxyl group is one of the most important functional groups of naturally occurring molecules such as carbohydrates and nucleic acids. These are complex alkanols but our concern in this unit are simple alkanols which are made from petroleum-derived hydrocarbons.

2.0 OBJECTIVES

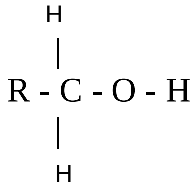
At the end of this unit you should be able to:

- classify alkanols into primary, secondary or tertiary groups.
- enumerate the sources of simple alkanols,
- describe the process involved in the local production of ethanol.
- list the uses of ethanol.

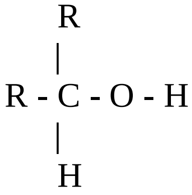
3.0 MAIN CONTENT

3.1 Classification of Alkanols

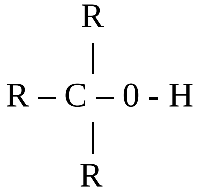
Alkanois are classified as primary, secondary or tertiary depending on whether the OH functional group is attached to a primary, secondary or tertiary carbon atom e.g



$$\mathrm{R - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - O - H}$$



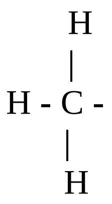
$$\mathrm{R - \underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}} - O - H}$$



$$\mathrm{R - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}} - 0 - H}$$

Primary (1°) secondary (2^{o}) tertiary (3^{o})

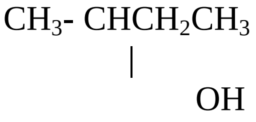
Where R = alkyl group



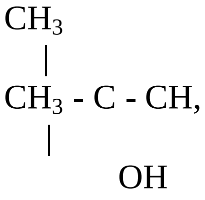
$$\mathrm{H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} -}$$

or CH_3- or H_3C-

$CH_3\ CH_2\ CH_2\ CH_2OH$



$$\mathrm{CH_3 - \underset{\underset{OH}{|}}{CH}CH_2CH_3}$$



$$\mathrm{CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH,}$$

butan-l-ol (1°) butans2- ol (2°) 2-methylpropan-2-ol (3^0)

SELF-ASSESSMENT EXERCISE

Three structural isomers of $C_4F1_{12}0$ are represented above. There is one more isomers alkanol not shown, can you draw and name it? (Hint: it is a 1° alkanol).

In-general, the characteristic of primary alkanols is CH_2OH; secondary alicanols is $\rightarrow CHOH$ and tertiary alkanol $\rightarrow COH$.

3.2 Sources of Alkanols

3.2.1 General methods of preparation

(a) Hydrolysis of halogenoalkanes or alkyl halides: Alkyl halides are compounds formed by replacing one of the hydrogen of an al/cane with a halogen (Cl or Br or I). When allcylhalides are treated with dilute aqueous sodium hydroxide, the halogen is replaced by - OH groups thus forming an alkanol.

$$R - CI + Na' + OH^- \longrightarrow R - OH + NaCl$$

e.g. $CH_3CH_2CI + NaOH \longrightarrow CH_3CH_2 - OH + NaCI$

ethyl chloride ethanol

(b) Hydration of alkenes: Alkenes react with steam when passed over phosphoric (v) acid catalyst at 300^{O}C and 70 atmosphere. For example.

$$CH_2 = CH_2 + H_20 \xrightarrow[300^OC + 70 \text{ aims}]{H_3PO_4} CH_3 - CH_2 - OH$$

The process, as shown in the equation, is used industrially for the production of ethanol and some higher alkanols.

3.2.2 Manufacture of Alkanols

(a) Methanol: Methanol is manufactured from mixture of carbon (II) oxide and hydrogen (obtained from either water gas or synthesis gas) in the presence of a catalyst.

$C_{coke}. + H_20_{(g)} \longrightarrow CO + H_2$ (water gas)

CH_4 (natural *gas)* + $H_20_{(8)} \longrightarrow$ CO 4 3H, (synthesis gas)

$$CO + 2H_2 \xrightarrow[400^OC \text{ and } 300 \text{ aims}]{H_3PO_4} CH_3OH$$

(b) Ethanol

(i) From ethene: The major source of ethanol industrially is by hydration of alkenes as described in section 9.3.1(b)

(ii) By fermentation: The fermentation process of obtaining ethanol from starch materials is still popu

Fermentation is the decomposition of complex organic compounds e.g. carbohydrates, into simpler compounds through the action of enzymes.

Materials such as, sugar, rice, guinea-corn, cassava, maize, potatoes, wheat, barley, etc. can be used as the source of glucose from which the ethanol is derived.

- From starchy materials: The material is crushed and treated with steam to extract the starch from them. Malt, made from partially germinated barley, is added and then kept at about 50°C for one hour. The enzyme diastase, present in the malt, catalyses the conversion of starch into maltose.

$$2(C_6H_{10}0_5)n + nH_20 \xrightarrow{\text{diastase}} n\ C_{12}H_{22}O_{11}$$

starch maltose

Yeast .s then added at room temperature. This causes fermentation, the enzyme maltase in the yeast, converts the maltose to glucose and another enzyme zymase in yeast, then decomposes the glucose into ethanol and carbon (iv) oxide.

$$C_{12}H_{22}0_{11(aq)} + H_20 \xrightarrow{\text{maltase}} 2C,H,_2O_{6(aq)}$$

glucose

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

Ethanol

- From molasses: In countries like Brazil, USA; where the production of sugar cane is high, the main raw material for ethanol production is molasses, a syrupy liquid that remains after the crystallization of sugar. It contains sucrose, a type of sugar. When molasses is mixed with yeast, the enzyme in vertase in yeast, converts the sucrose to two simple isomeric sugars, glucose and fructose, which are both fermented into ethanol by zymase.

$$C_{12}H_{12}0_{11} + H_20 \xrightarrow{\text{invertase}} C_614_{12}0_6 + C_6H_{12}0_6 \xrightarrow{\text{zymase}} 4C_2H_5OH + 4CO_2$$

Glucose fructose

- From palm wine: In some parts of Africa e.g. Nigeria, Ghana, South Mica, local gin is obtained by fermenting palm wine which is rich in sugar. Fresh palm wine contains sugar and yeast which on storage in large earthenware pots or drums for 3-4 days, is fermented to ethanol. The resulting solution is then distilled to obtain the clear ethanol usually called gin. *(ogogoro* in Nigeria).

(c) Purification of ethanol

The ethanol obtained from the fermentation process can only give a maximum concentration of 18%, since the yeast cells die above this concentration. For commercial *use,* ethanol is required in various compositions and to achieve further concentration and purification, fractional distillation is employed.

For alcoholic beverages, different concentrations of ethanol is used and their flavour varies with raw material fermented. Table 9.1 shows the percentage of ethanol and the method of preparation.

Table 9: I Kinds of alcoholic beverages

Raw material	**Alcohol beverage**	**% Ethanol (v/u)**	**Method of preparation**
Barley, wheat	Beer e.g. star	3 -8	Fermentation
Grapes/ Rice	Wines	8 - 18	Fermentation
Barley, wheat, Grapes	Whisky /spirit/brandy	30- 60	Fermentation and distillation

Commercial ethanol is sold as pure spirit or rectified spirit or methylated spirit containing 95% ethanol. When sold to the public, 5% methanol, which is toxic, is added to prevent it being consumed as a drink.

3.3 Uses of Ethanol

(a) It is used as solvent for resins, varnishes, polishes, liquid soaps, perfumes, drugs and paints
(b) It is used as a fuel, either by itself or mixed with petrol, in racing cars and rockets
(c) It is used as an anti-freeze in automobile radiator
(d) It is present in many alcoholic beverages
(e) It is used for sterilization and preservation of specimens and food
(f) It is used as raw material in the manufacture of chemical e.g. ethanal, trichloromethane, ethoxyethane

4.0 CONCLUSION

In this unit you have learned about the group of compounds known as alkanols. You should also have learned about the classification and the principal sources of alkanols. You need to be aware of the fermentation process for the conversion of various raw materials to alcoholic beverages. In addition you should be able to enumerate the various uses of ethanol as the most important compound of the alkanol series.

5.0 SUMMARY

- What you have learned in this unit concerned an important homologous series, the allamols which are characterized by the presence of the OH functional group.
- Alkanols are classified into primary, secondary and tertiary alkanols depending on the position of the - OH group.
- The main source of alkanols is by hydration of alkenes; however the most important compound of the series, ethanol, can also be obtained by the fermentation process. Alkanols, particularly ethanol plays an important role in our lives owing to its numerous uses.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Write and name all the structural isomers of $C_sH_{i3}O$ which are alkanols. Indicate whether they are primary, secondary and tertiary alkanols.
ii. Describe the fermentation process for the production of ethanol.

7.0 REFERENCES/FURTHER READING

Bajah, ST., Teibo, B.O., Onwu, G. and Obikwere, A. *(2002)Secondary Secondary Chemistry Textbook* 3. Lagos. Longman Publishers.

UNIT 5 ALKANOLS II CHARACTERISTICS ALKANOLS OF

1.0 INTRODUCTION

In unit 9 you were introduced to the Chemistry of alkanols, a homologous series characterised by the -OH functional group. You learned about the classification of alkanols into primary, secondary or tertiary based on the position of the -OH group in the molecule. The sources of alkanols were discussed. However of principal interest is the methods used for the production of the most important member of the series, ethanol. Ethanol is produced mainly by hydration of ethene and the fermentation of glucose.

In this unit you will learn about the characteristics of alkanols. Like all organic compounds, the behaviour of alkanols is controlled by the-OH functional group. The -OH is polar in nature.

2.0 OBJECTIVES

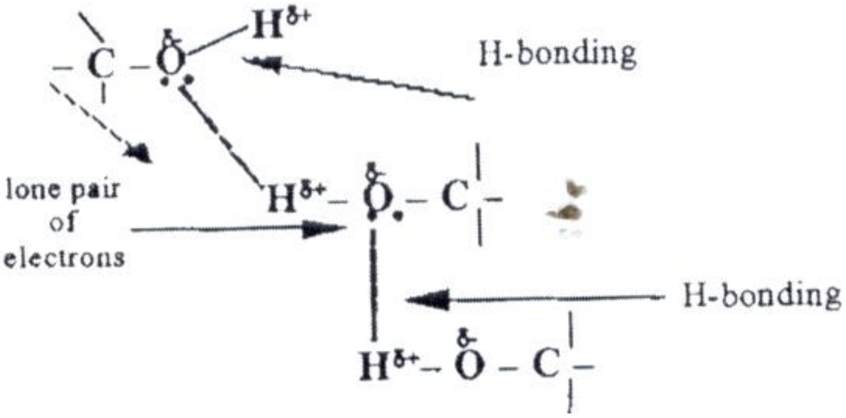
At the end of this unit you should be able to:

- use hydrogen bonding to explain the variation in physical properties of alkanols
- discuss the basic reactions of alkanols
- describe the laboratory test for allcanols

3.0 MAIN CONTENT

3.1 Intermolecular Hydrogen Bonding in Alkanols

In unit 5, volume I you learned about the secondary types of bonding to exist in organic molecules, one of these is hydrogen bonding. Reran that hydrogen bonding exist only in compounds with groups that have highly electronegative atoms, like 0, N(with lone pair of electrons) attached to hydrogen. The -OH of alkanols lead to intermolecular hydrogen bonding between alkanol molecules



H-bonding is a stronger bond than the Vander Waal's forces, which are known to hold molecules together. Hence, alkanols exist as aggregates of molecules and not as individual molecules existing in isolation.

3.2 Physical Properties of Alkanols

(a) The physical properties of Drano's show the normal gradation associated with any homologous series. They are, however, considerably affected by hydrogen bonding between alkanol molecules. This causes some degree of intermolecular association in alkanols, as it does in water, so that boiling points of alkanols are higher than those of other classes of compounds with similar molecular mass in which there is no H- bonding. For example:

Compound	Molecular Mass	B. p °C
benzene (end	78	80
pentane te1112)	72	36
chloropropane (efi,C1)	79	47
Ethoxyethane (C41-1100)	74	35
*butanal (C4110)	72	76
*butm4-ol (C411,30)	74	118
*water (Hp)	18	100

*Note: * hydrogen bonding exists in these molecules, hence their high boiling point*

(b) The - OH group is polar and as expected alkanols are soluble in water. Lower members of the series are very soluble in water, however, solubility decreases as the alkyl group or molecular mass increase within the series. This is because the organic character (determined by the alkyl group, R) increases with molecular mass down the series when compared to the relative polar character (determined by the —OH group).

3.3 Chemical Properties of Alkanols

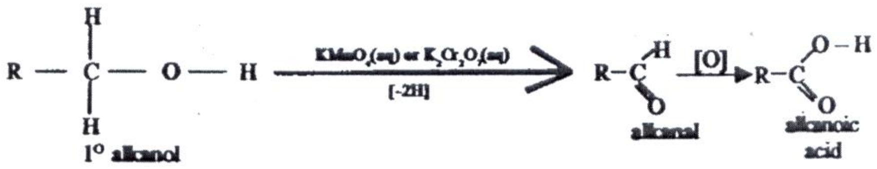
Primary and secondary, but not tertiary alkanols can be easily oxidised, and most alkanols also undergo elimination (dehydration) and substitution reactions. The substitution reaction can be of two kinds. The hydrogen atom of the hydroxyl group can be substituted with the 0-H bond being split. In these reactions the alkanols act as an acid and the R-0^- ion is formed as intermediate i.e. $ROH \rightleftharpoons RO^- + H^+$

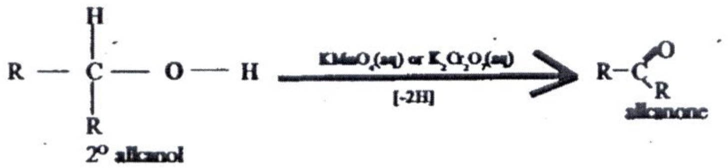
Alternatively, the whole hydroxyl group may be substituted with the C-0 bond splitting. Direct substitution of the hydroxyl groups is not easy but it is facilitated in acid solution.

3.3.1 Oxidation Reactions

Primary and secondary alkanols are oxidised, by dehydrogenation, to form alkanals and alkanones respectively. Alkanals and alkanones are two important homologous series of organic compounds. However, discussions on them is beyond the scope of this programme. The oxidation can be achieved using oxidising agents such as $KMnO_4$ or $K_2Cr_20_7$.

The reactions involve the loss of the -OH hydrogen together with a hydrogen atom from the adjacent alkyl group. With primary alkanols, the initial alkanal product may be oxidised further to an alkanoic acid, if excess oxidising agent is used, but alkanones cannot be readily oxidised.

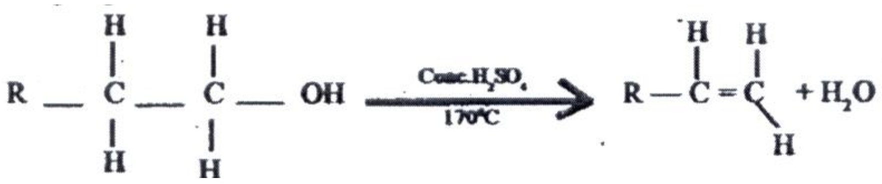




Tertiary alkanols have no hydrogen atom on the alkyl group adjacent to the hydraxyl group and they are, therefore, not readily oxidized.

3.3.2 Examination (dehydration) Reactions

Alkanols are readily dehydrated (removal of H_2O) on heating with conc, tetraoxaolphate (IV) acid to give alkanes. The best yields of alkenes are obtained at 170°C and by using excess concentrated H_2SO_4. This dehydration is only possible in molecules containing at least one hydrogen atom on the carbon atom next but one to the – OH group.



When the alkanol is present in excess, however, the dehydration occurs between two molecules to form another class of compounds called alkoxy alkanes.

$$2R-CH_2OH + H_2SO_4 \xrightarrow{140^\circ C} R-CH_2OCH_2R + H_2O$$

Alkanol **alkoxyalkane**

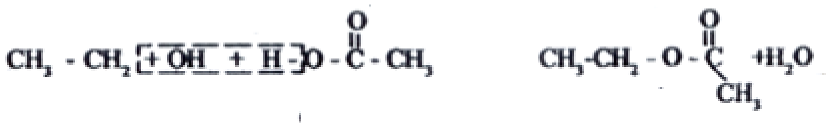
3.3.3 Substitution Reactions

(a) Reaction with sodium: the acidic at of die -OH group shows up in their reaction with reactive metals, such as sodium, to liberate hydrogen gas.

$2R\text{-}0-H + 2Na \longrightarrow 2R - 0^- Na^+ + H_2$

(b) Esterification: alkanols react with alkanoic acids to form alkanoance a series of compounds to be studied in Unit 12.

Alkanoates are commonly called coster (hence the term esterification for this reaction) and are usually sweet-smelling liquids. The reaction involves the replacement of the –OH group of alkanols, thus showing a basic character. The reactions are both slow and reversible; and is therefore catalysed using small amounts of strong acids e.g. H_2SO_4.



Alkanol (ethanol)	alkanoic acid (ethanoic acid)	alkanoic ethyl ethanoic)

3.3.4 Iodoform Test

Ethanol and methanolreact with a mixture of iodine and sodium hydroxide to form a yellow precipitate of triodomethane CH_3 (Iodoform).

$$CH_3CH_2OH + 4I_2 + 6NAOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2P$$

This reaction is used to confirm the presence of certain types of alkanols namely, methanol, ethanol and other alkanols with the -OH group on a carbon atom adjacent to a methyl (-CH) group.

3.5 Laboratory Test for Alkanols

The presence of alkanols is confirmed based on the differences in the rate of reaction of primary, secondary and tertiary alkanols With Lucas reagent (mixture of conc.HCI and Znc1_2).

$$R - OH \xrightarrow[ZnCl_2]{Conc.\ HCl} R - CI$$

At room temperature, a tertiary alkanol reacts with Lucas reagent to give immediately turbidity (cloudy) of the chloride. Secondary alkanols also react at room temperature, however, the reaction is a lot slower and the 'tertiary only appears after about 5minutes. Primary alkanols does not react with Lucas reagent at room temperature at all, however, the turbidity can be observed when the reaction mixture is heated.

4.0 CONCLUSION

In this unit you have learned about the properties of alkanols. You have learned about the influence of hydrogen bonding on the physical properties of alkanols. Furthermore, you should have learned that the reactivity of the alkanols is centered around the -OH functional group. The hydroxyl group, though essentially neutral, but in the presence of certain reagents can undergo a series of reactions such as its action with sodium or potassium which is an important reduction reaction, it also gives an important reaction with Phosphorous pentachloride and forms esters with organic acids.

5.0 SUMMARY

In this unit you have learnt about the important characteristics of alkanols and how the functional group -OH plays an important role in the chemical reactivity of alkanols. You will in the next unit, study the chemistry of alkanoic acids which will focus fundamentally, on such aspects as its sources, methods of preparation, physical/ chemical properties etc.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Explain why alkanols exist as aggregate of molecules and not as isolated or individual molecules.
ii. Why are alkanols soluble in water, why does the solubility in water decrease as you go up the series.
iii. Given a mixture of primary, secondary and tertiary alcohols, how can you proceed to distinguish between the-various classes.

7.0 REFERENCES/FURTHER READING

Baja, S. T. Teibo, B.O, Onwu G., and Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook 3.* Lagos. Longman Publishers.

Osei Yaw Abaltio (2002)4tew *School, Chemistry.* Onitsha. Africanan Tap Publishers.

MODULE 3

UNIT 1 ALKANOIC ACIDS

CONTENTS

1.0 INTRODUCTION

Alkanoice acids are groups of manic compounds which contain the -COOH group fisted to a hydrogen atom or to an alkyl group. The old name for members of this homologous series is carboxylic acids The names of members of the sales are obtained by replacing the '-e' of the corresponding alkane by '-oic' and add the word 'acid' Members of the series can be it represented by the general molecula formula of C_nH_{2n+1} COOH where $n \geq O$. They are sometimes called fatty acids because some of them are found in natural Eats oils.

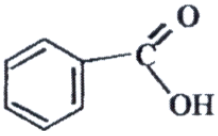
The first five mambas of the alkanoic acid series are shown in Table 11.1 below:

Table 11.1

Molecular Formula	*Structural formula*	*1UPAC muse*
CH_20_2	HCOOH	methanoic aid
$C_2H_40_2$	CH_3COOH	ethanoic add
$C_3H_60_3$	CH_3CH_2CO0H	propanoic acid
$C_4H_30_2$	$CH_3CH_2CH_2C00H$	butanoic acid
$C_5H_{10}0_2$	$CH_3CH_2CH_2CH_3COOH$	pentoole acid

Alkanoic acids are sometimes represented as R-COOH, where R = alkyl group. Older names specific " alkanoic acids refer to the origin or use of the acid, e.g. methanoic acid vas first made from ants (Formica = ant) and is called formic acid; ethanoic acid occurs in vinegar (aces sour) and is called *acetic acid.*

Apart from the aliphatic acids, aromatic adds such as benzoic acid are also important members of this series.



benzoic acid, an aromatic acid

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- name *using* the IUPAC nomenclature of simple alkanoic acid
- explain how hydrogen bonding affects the properties of alkanoic acids
- explain the methods of preparation and properties of alkanoic acids

3.0 MAIN CONTENT

3.1 Sources of Alkanoic Adds

3.1.1 Natural Sources

Several members of the alkanoic acid series are widely distributed in nature and found in living organism. For example, metheistic acid was first obtained from ants; ethanoic acid is present in vinegar and is responsible for its sour taste; butanoic acid has been isolated from human sweat. Higher alkanoic acids, such as citric acid. tartaric acid, are known to be present in several types of fruits and vegetables.

3.1.2 General Methods of Preparation

(a) oxidation of primary alkanols

Primary alkanols are oxidised by oxidising agents, such as potassium tetraoxomanganate (VII), potassium heptaoxochromate (VI) to alkanoic acids. The reaction is usually carried out by refluxing excess of the oxidising agent with the Akanol.

$$R — CH_2\ OH \longrightarrow R — COOH + H_20$$

Note: [O] *represents the axidising agent*

b) Hydrolysis of nitrite

The acid catalysed hydrolysis of utile with water, yield ataxic acid. For example ethanenitille can be hydrolysed to ethanoic acid in the presence of small amount of tetraoxosulphate (VI) acid.

$$\underset{\text{ethanonitrile}}{CH_3CN} + \longrightarrow CH_3COOH + NH_3$$

SELF-ASSESSMENT EXERCISE

(a) Find out the names of the alkanoic acids present in lemons, grapes and SOW milk.
(b) Write equation to show the preparation of butancic acid from butanol

3.2 Characteristics of Alkanoic Adds

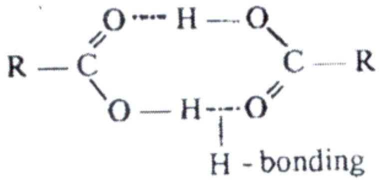
3.2.1 Physical Properties

(a) Lower members of the alkanoic acid series, such as methanoic acid and ethanoic acid, are completely miscible in water. Solubility, however, decreases with higher members of the series. In general, alkanoic acids are mere soluble in water, (a polar solvent) than the corresponding Alkanols with the same number of carbon atoms. This is parity due to the high polarity of the $C^{\delta+}$- O^{δ} and O^{δ}- H^{δ} bonds, which makes it easier for the alkanoic acid molecule to bond readily with water molecules hence increased solubility. With higher members of the series, however, the hydrocarbon component (R groups which are organic) becomes larger than the polar component in the molecules, hence the decrease in solubility.

(b) Alkanoic acids have many higher bailing points than other compounds with comparable relative molecular mass e.g.

	Relative Molecular Mass	boiling point
ethanoic acid	60	118^{o}C
propan-l-ol	60	97^{o}C
butane	58	-1^{o}C

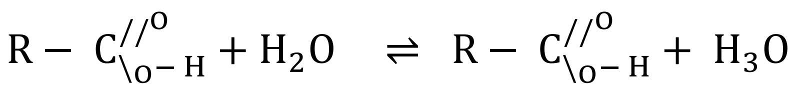
The high boiling points of alkanoic acids is *as* a result of strong intermolecular hydrogen bonding that exist between the molecules. In fact lower members of the series do not exist as single molecules but as dimers (as shown below), giving then an usually higher molecular mass than expected.



The hydrogen bonding between alkanoic acid molecules and voter molecules, also partly explains their high solubility in water.

3.2.2 Chemical Properties

(a) Acidity: Due to the polar nature of the bonds in alkanoic acids they ionise in water as follows:



$$R- C\genfrac{}{}{0pt}{}{//^{O}}{\backslash_{O}- H} + H_2O \rightleftharpoons R- C\genfrac{}{}{0pt}{}{//^{O}}{\backslash_{O}- H} + H_3O$$

However, alkanoic acids *are weaker* acids than mineral acids, such as hydrochloric acids, but they are very much stronger than alkanols. The strength of any alkanoic acid depends on the equilibrium position of the equation above. The stronger the acid the further to the right will be the equilibrium position so that the acid strength will depend on the readiness with which the -0-H bond will split in the presence of water.

SELF-ASSESSMENT EXERCISE

Can you explain why alkanols, R-OH are weaker acids than alkanoic acids, R-COOH.

(b) Formation of salts: Alkanoic acids react with bases and trioxocarbonate (iv) to form salts. Thus it

(i) reads with trioxocarbonate (iv) and hydrogen triomicathanate(iv) to give salts of the add with liberation of carbon(iv) oxide.

$$2RC00H + Na_2CO_3 \rightarrow 2RCOONa + H_20 + CO_2 \uparrow$$

(ii) reacts with bases or alkalis to form salts of the acids and water. This is an acid-base neutralization.

$$RCOOH + NaOH \rightarrow RCOO^-Na^+ + H_20$$

In the reaction above, alkanoic acids behave like mineral acids, exhibiting their acidic property. Alkanols do not undergo these reactions because they are weaker acids.

(c) Formation of esters (esterification): Alkanoic acids react with alkanols to form alkanoates (esters), the H-akin of the carboxyl group is replaced by an alkyl group e.g.

$$\underset{\text{alkanoic acid}}{R\text{--}COOH} + \underset{\text{alkanol}}{R^1 OH} \rightleftharpoons \underset{\text{alkanoate}}{R\text{-}COOR'} + \underset{\text{water}}{H_20}$$

The reaction is usually catalysed with mineral acids e.g. HG or 11_2SO_4. This reaction is commonly referred to as esterification Alkanoates or esters is an important homologous series and is the subject of our discussion in the next unit.

(d) Reduction: Alkanoic acids can be reduced to primary alkanols using a special reducing agent called lithium aluminium hydride, $LiAlH_4$.

$$R\text{-}COOH \xrightarrow{LiAlH_4,HCI} R\text{ - }CH_2OH$$

This malefic.] react on is the reverse process of the oxidation of primary alkanols, used for producing alkanoic acids (see section 11.2.2 of this unit).

3.3 Laboratory Test for Alkanoic Acids

The presence of the alkanoic acid functionality is usually confirmed in the laboratory by utilizing its acidic properties. As stated in Section 3.2 of this unit, alkanoic acids react with trioxocarbonate(iv) or hydrocarbonates to liberate carbon(iv) oxide. This is the laboratory test for the COOH group present in all alkanoic acids. The evolution of the CO_2 gas is used as evidence of the presence of alkanoic acids

$$R - COOH + NaHCO_1 \rightarrow R - COONa + H_20 + CO_2\uparrow$$

3.4 Uses of Alkanoic Acids

a) Methanoic acid is used in dyeing electroplating, taming and in coagulating rubber.
b) Ethanoic acid is used as a raw material in the
   - manufacture of cellulose ethanoate (used for packing, in varnishes, in the filter tips of cigarettes and in synthetic fibres).
   - manufacture ethanoic anhydride which is used in aspirin.
c) Ethanoic acid is an important organic solvent
d) Higher alkanoic acids are used for making soaps and detergents.

4.0 CONCLUSION

In this unit you have learned about an important class of organic compounds called *amok acids. You have learned about their presence in living organisms and how they are male in the laboratory. You should also have learned about the polarity of the functional group and the influence of H-bonding on the physical properties of alkanoic acids. You should be aware of the acidic nature of the -OH bond of the *acids* and bow it influences its characteristic reactions.

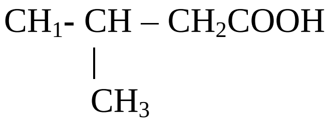
5.0 SUMMARY

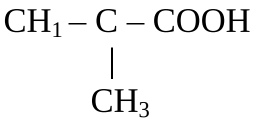
What you have learned in this unit concerns the chemistry of the -COOH functional group as present in the alkanoic acid series. It has served to underscore the importance of functional groups in understanding organic chemistry in general, as specific characteristics of *the classes* of organic compounds.

6.0 TUTOR-MARKED ASSIGNMENTS

Give the IUPAC name of the following compound

CH_1
|


$CH_1-\underset{\overset{|}{CH_3}}{CH}-CH_2COOH$


$CH_1-\underset{\overset{|}{CH_3}}{C}-COOH$

b) Write the equations for the following reactions
(i) ethanoic acid with calcium trioxocarbanate (iv)
(ii) ethanoic acid with calcium hydroxide
(iii) ethanoic acid with ethanol.

7.0 REFERENCES/FURTHER READING

Bajah, S.T., Teibo, B.O., Onwu, *G.*, and Obikwere, A. (2002). *Senior Secondary Chemistry*- *Textbook 3*. Lagos. Longman Publishers.

Osei Yaw Ababio (2002)New *School Chemistry*. Onitsha. Africana-Fep Publishers.

UNIT 2 ALKANOATES

CONTENTS

1.0 INTRODUCTION

Alkanoic acids form a variety of important derivatives one of which is the alkanoates. The common name for alkanoates is esters. Alkanoates are formed from alkanoic acids by replacing the - OH of alkanoic acids with-OR group (where R = alkyl group). They are represented by the general formula, $RC00R^1$ or $C_oH_{2n-1}COOCnH_{2n-1}$ (where n 0).

The IUPAC nomenclature for members of the series are derived from the alkanols (WON) and the alkanoic acid (RC00H) from which the alkanoates are formed. The alkanoi portion. R^I is named first as alkyl and a space is left, which is followed by the alkanoic acid portion R^1 COO. named as alkanoate. For example.

(a) CH_2 .$CCOCH_3$, = methylethanoate indicating that it is formed from methanol as the alkanol and ethanoic acid (as the alkanoic acid)

(b) $CH_3CH_2COOCH_2CH_3$ = ethyl propanoate indicating that it is formed methanol (as the alkanol and propanoic acid (as the alkanoic acid).

Naturally: occurring esters are called fats and oils, formed from long chain alkanole acids it the ester are liquids at room temperature, they are called oils. Whereas if they are solids at room temperature they are called fats. Examples of these are the fats it allow from cons cocoa butter from exam and oils palm oil from oil palm, groundnut oil from groundnut, castor oil from castor plant) which are used for cooking are source of energy and in the manufacture of soaps.

Lower alkanoates are known for their characteristic sweet strong aroma and are found in many flower, and fruits e.g. methyl butanoate in pineapple, pentyl ethanoate in banana. The aroma of alkanoate IS sometimes used to confirm their presence.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

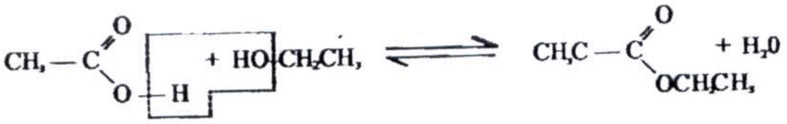
- identify and name alkanoates based on their formula
- identify some of the natural sources of alkanoates.
- explain esterification as the preparatory route to alkanoate.
- explain the characteristics of alkanoates.

3.0 MAIN CONENT

3.1 Preparation of Alkanoales: Esterification

Recall from unit 1, the esterification process. This process is the principal route for making alkanoates. The direct reaction of alkanoic acid and alkanols in the presence of catalytic of a mineral acid is known as esterification.

For example, ethyl ethanoate is prepared by heating ethanoic acid and ethanol with concentrated tetraoxo sulphate (vi) acid as catalyst.



Ethanoic acid ethanol ethyl ethanoate

Esterification is an equilibrium process, and for production of ethyl ethanoate, the forward and backward raction occur at about the same rate. A convenient procedure for making ethylethanoate in good yield, is to run a mixture of ethanoic acid and ethanol into a hot mixture of ethanol (excess) and concentrated tetraoxosulphate (vi) acid at the same rate as the alkanote distills off. The solution obtained from the distillation is shaken with concentrated trioxocabonate (iv) to remove acids, and with concentrated calcium chloride solution to remove ethanol. The resultant solution is then dried over anhydrous calcium chloride, and the ethyl ethanoate is obtained pure by redistillation.

3.2 General Characteristics of Alkanoates

3.2.1 Physical Properties

Alkanoates are coldness lipids or solids, sparingly soluble in watt Most of than have a characteristic fragrant odour or sweet smell and many of them occur naturally. The fragrances in flowers and fruits attracts the insects and animals which are responsible for the pollution of flowers and dispersal of seeds.

3.2.2 Chemical Properties

Alkanoates are generally not very reactive but can be hydrolysed to their precursor alkanoic acids and alkanols; and reduced to primary alkanols.

a) Hydrolysis of alkanoates: Alkanoates are hydrolysed very slowly by boiling with water to give the component alkanoic acids and alkanols. The reaction can be made faster by catalyzing the hydrolysis with acids or bases.

$$CH_3COOC_2H_5 + H_20 \rightleftharpoons CH_3COOH + C_2H_30H$$

The acid – catalyzed process is the reverse of esterification and, as it is reversible, an excess of acideic solution is required to give a good yield of alkanoates.

The base–catalysed hydrolysis is a more efficient process for the alkanoate ion formed, does not react appreciably with alkanols so that the reaction goes almost to completion e.g.

$$R - COOR^1 + OH^- \rightarrow R - C00^- + R^1 - OH$$

alkanote from base alkanoate ion

This alkaline hydnalysis process commonly called sapoafication is used for the conversion of naturally occurring esters (alkanoales) into soaps The process of soap making by saponification will be dismissed in details in the next unit

(b) Redunction of alkanoates: Alkanoates can be reduced to primary alkanols more easily than alkanoic acid. Lithium aluminum hydride and catalytic hydrogenation are both effective catalysts for reduction

$$R - COOR^1 \xrightarrow[H_2/Ni]{LiAIH_4 \text{ or}} R - CH_2OH + R^1 - OH$$

Alkanoate primary alkanol

$$CH_3C00C_2H_3 + 4[H] \rightarrow 2C_2H_5OH$$

from reducing agent

3.3 Uses of Altamonte

(a) A large member of alkanoates are used as perfume and flavourings. For example ethyl methanoate obtained from room; 3-rnethylbutyl ethanoate obtained from pear, and ethyl butanoate obtained from pineapple are all used in this way for perfumes and few flavouring

(b) Ethyl ethanoate is a good solvent

(c) Certain useful *waxes* are composed mainly of alkanoates e.g. beeswax, $C_{15}H_{3I}COOC„H_{63}$

(d) Alkanoates of trilydric alkanols and alkanoic acids are of great, importance in making soap and propane 1,2,3-triod (glycerol)

4.0 CONCLUSION

In this met you ban leaned about alienates a class of again compounds known for their sweet smelling Invents. You should have also trained that the odour of flowers and fruits are largely due to the alkimoates present in them. In addition, you should be familiar with the processes of esterification and saponificance. You need to be aware of the numerous uses and importance of alkanons.

5.0 SUMMARY

What you have leaned in des unit concerns the chemistry of alkanoates and the importance of this class of compound as flagrant; and flavouring. Alkanoates are the basic raw material for the manufacture of soaps which will be discussed in as in the next unit.

6.0 TUTOR-MARKED ASSIGNMENTS

i) Write the structure and name four alkanoates with the general fomula $C_4H_8O_2$

ii) describe the esterification process for the preparation of ethyl ethanoate

iii) write the equation for the hydrolysis of methyl ethanoate.

Bajah, S.T., Teibo, B.O., Onwu, *G.*, and Obikwere, A. (2002). *Senior Secondary Chemistry- Textbook 3.* Lagos. Longman Publishers.

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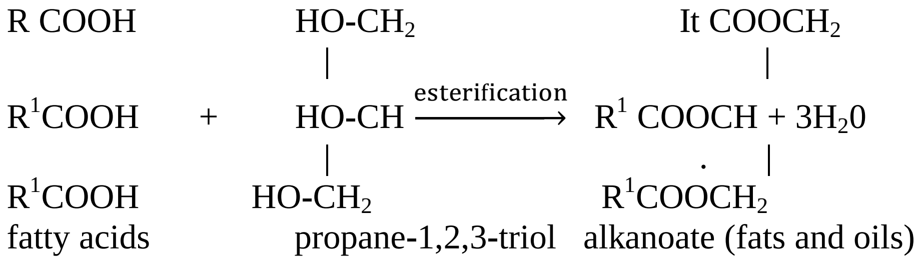
UNIT 3 FATS, OILS AND AMINO ACIDS

CONTENTS

1.0 INTRODUCTION

Fats and oil are naturally occurring alkanoates formed from the trihydric alkanol, propane – 1,2,3- triol (commonly known as glycerol) and long-chain alkanoic acids (commonly known as fatty acids) with C_{12} to C_{24} carbon atoms. A trihydric alkanol is one with three hydroxyl group (-OH) in the molecule; hence during esterification, each molecule; hence during esterification, each molecule of the trihydric alkanol reacts with three molecules of fatly acids to give the fats and oils as follows



$$\begin{array}{lcccl} R\ COOH & & HO\text{-}CH_2 & & It\ COOCH_2 \\ & & | & & | \\ R^1COOH & + & HO\text{-}CH & \xrightarrow{esterification} & R^1\ COOCH + 3H_20 \\ & & | & & .\ \ | \\ R^1COOH & & HO\text{-}CH_2 & & R^1COOCH_2 \\ \text{fatty acids} & & \text{propane-1,2,3-triol} & & \text{alkanoate (fats and oils)} \end{array}$$

This esterification process occurs naturally in plans and animals to give fats and oils, which are generally referred to as lipids. Fats are solids, at roan temperature, usually of animal origin Mile ads we liquids, at room temperature, mainly of plant origin. The fatty acids commonly found in lipids can be subdivided into saturated fatty acids (have no doubt bond in Sir hydrocarbon chain) and unsaturated fatty acids (have one or more double bond in their hydrocarbon chain). Examples of these fatty acids are given below (Table 13.1):

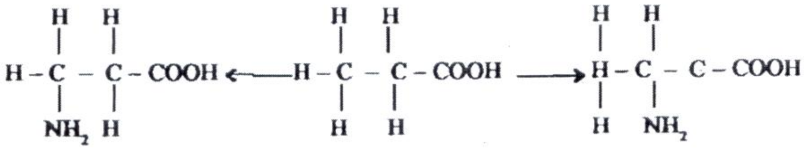
Table 13.1

Common Name	**Source**	**Formula**	**IUPA nomenclature**
Palmitic acid	oil palm	$CH_2(CH_2)_{14}C00H$	hexadecanoic acid
Stearic acid	tallow (animal fat)	$CH_2(CH_2)_1COOH$	octadecanoic acid
Oleic acid	olive or peanut oil	$CH_2(CH_2)_7CH=CH(CH_2)_7COOH$	Ociadec-9-enoic acid
Linolcic acid	vegetable oil	$CH_2(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	Octadeca-9,12-dienoic acid

Amino acids at substituted alone acids in which dm hydrogen atom(s) in the alkyl groups Moe been replaced by amino group (-NH_2 group).

For example

Ethanoic acid **2-amino ethanoic acid**
an amino acid commonly celled glycine



3mithampance acid propanoic acid 2- amino propanoic acid

Amino acids are impotent substituted alkanoic acids for they are the components parts of proteins, which occur widely in all plants and animals. Proteins will be part of our discussion in Unit 14.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- identify fats and oils as alkonoates.
- recall some of the natural sources of fats and oils.
- describe the saponification process for the manufacture of soap.
- describe the process of hardening of
- compare properties of soap and detergent.
- identify the functional groups in amino acids.

3.0 MAIN CONTENT

3.1 Sources of Fats sad Oils

Fats and oils are widely distributed in nature. They are used by man for cooking, as source of energy and for the manufacture of soap. Animal fats and oils at usually obtained by treating the animal tissues with hot water. This breaks down the cell walls and allows the molten fats or oil to rise to the surface of water. Tallow is obtained in this way from beef or mutton (remember the sance obtained when meat is bailed in water); pure lard from pigs. Vegetable oils are usually obtained by pressing the plant to squeeze out the oil or both extraction with organic solvents.

Table 13. 2 shows some common fats and oils; their natural sources and procedure countries.

	Fats or oils	Natural source	Producer countries
1.	Groundnut oil	Groundnut	Nigeria, Gambia
2.	Palm oil	Oil palm	Nigeria, Malaysia
3.	Coconut oil	Cocnut tree	Nigeria, Malaysia
4.	Cotton seed oil	Cotton	Nigeria, USA, Egypt
5.	Soya been oil	Soya tree	Nigeria, USA
6.	Castor oil	Castor seed	Nigeria, Malaysia
7.	Palm kenel oil	Oil palm	Nigeria, Malaysia
8.	Sunflower oil	Sunflower	Nigeria, Kenya
9.	Tallow fat	Sheep and cow	Argentina, USA, Australia
10.	Lard fat	Pigs	USA, China
11.	Coca butter	Cocoa	Brazil, Nigeria, Ghana
12.	Wool grease	Sheep	Argentina, Australia

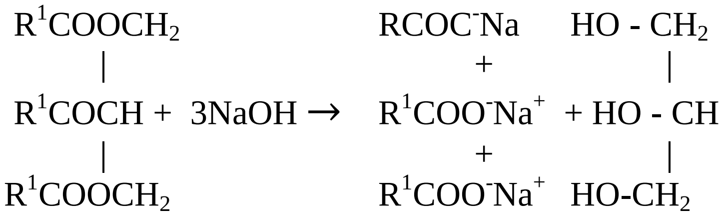
3.2 Hardening of Oils

Vegetable oils can be changed to fats by catalytic hydrogenation (addition of hydrogen to the double bond present in the hydrocarbon chain of the oil). Margarine (e.g. Moe Band) is made by this proms. The oils, usually from plants such as oil palm, groundnut and soya-been are heated to about 180^{o}C in the presence of finely divided nickel, as catalyst, and hydrogen gas is bubbled in at 2-5 atmosphere. The hydrogen is added across the double bonds present in the unsaturated hydnxarbon chains of the oil. The product is a fat, which is then mixed with salt, vitamins, milk and other additives to form margarine.

3.3 Soap Manufacture: Saponification

Recall from unit 12 that saponification is the alkaline hydrolysis of alkanoates. Fats and oils, which are alkanoates of fatty acids, can be hydrolysed with caustic alkali to give propane – 1,2,3-triol and the corresponding sodium and potassium salts of the component fatty acid. These salts are the main constituents of soap. Sodium chloride is used to remove (salt out) the soap from the mother liquor, which is denser than the soap. After washing the soap free of excess alkali, different additives (dyes, perfumes) are then added to give varieties of soaps. The nature of the staring oil to determine the type of soap obtained.

$$\text{Fat or + caustic alkali} \xrightarrow{\text{saponification}} \text{soaps + propane-1,2,3-triol}$$



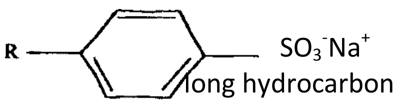
$$\begin{array}{lcll}
R^1COOCH_2 & & RCOC^-Na & HO - CH_2 \\
| & & + & | \\
R^1COCH + 3NaOH & \rightarrow & R^1COO^-Na^+ & + HO - CH \\
| & & + & | \\
R^1COOCH_2 & & R^1COO^-Na^+ & HO\text{-}CH_2
\end{array}$$

Soaps propane-1,2,3-triol (glycerol)

3.4 Detergents

These are substances which have the ability to clean an object such as soaps. Detergents are usually classified into two main types - soapy detergents and soapless detergents. The soapy detergents e g soaps are the sodium or potassium salts of fatty acids produced by the saponification of fats and oils, as described in Section 13.4

Soapier detergents *are* the alkyl benzene sulphonates, abbreviated as ABS.
A soapless detergent molecule is



R =

(ABS)

Like soap, soapless detergents are sodium salts of sulphonic acid to which an aromatic - alkyl chain is attached Soapless detergents are the more favoured clearing agents nowadays than the soapy detergents. They are available as liquids or solids and the raw materials for their manufacture are petrochemicals obtained firm refining crude oil.

Soapless detergents, are preferred because:

(a) they do not form scum with hard water and therefore retain their cleansing properties irrespective of the type of water used.
(b) they are neutral in water, whereas soapy decagons at slightly alkaline in water and thereat not Stable fix washing acid-sensitive fabrics
(c) they have wider applicants, in terms of removing various types of stains, than soapy detergent.

3.5 Use of Fats sod Ws

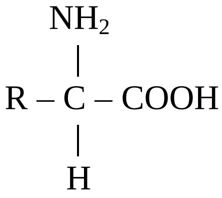
(a) As foodstuffs: most fats are consumed as food; together with carbohydrates, they provide source of energy for animals.
(b) In making soaps the fats and oils commonly used for making soaps are tallow, coconut on, bleached palm oil, soya bean oil and olive oil.
(c) In making candles: when tallow is hydrolysed under pressure it gives products used in making candles.
(d) In making glycerol: glycerol is the by-product obtained in the manufacture of soap. It is used in the manufacture of creams, medicine.
(e) In making paints: linseed oil is used for making oil paints.
(f) in making margarines: margarines is made by hardening oils and is a good substitute for butter.

3.6 Teats toe Fats and Oils

(a) Paper test: a drop of oil or melted fat on a piece of paper forms a translucent (allow light to pass through) grease spot.
(b) Sudan III test: to a mixture of oil and water add 4 to 5 drops of sudan III stain, a red stain confirms fats and oils.

3.7 Amino Acids

Amino acids are derivatives of alkanoic acids in which the hydrogen of the alkyl dual is replaced by the amino group (-NH_2). Each amino acid contains two functional groups, the catboxyl group (-COOH) and the amino group (-NH_2). It therefore has a general structure as follows.



$$R - \overset{\overset{NH_2}{|}}{\underset{\underset{H}{|}}{C}} - COOH$$

Amino acids are the basic structural units of proteins. All the amino acids obtained by hydrolysis of animal and plant proteins have the amino group attached to the carbon adjacent the carboxyl group. They are called ∝- amino adds mid twenty (20) of such amino acids have been isolated in nature. All proteins found in living organisms are combinations of these amino acids. You will learn more about proteins in the next unit

In aqueous solution, amino acids are neutral to litmus, but they can *act* as an acid, on account of the -COOH group, or as a base, on account of the $–NH_2$ group. Amino acids can therefore react with acids or bases to form salts.

Let is consider the following reactions:

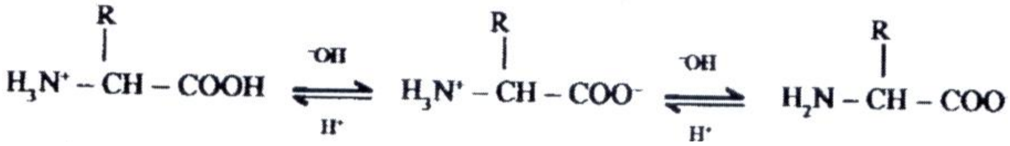
$$NH_2CH_2COOH + HCI \rightarrow CI^-NH_3CH_2COOH$$

$$NIL_2CH_2COOH + NaOH \rightarrow NH_2CH_2C00^-Na'' + H_70$$

In neutral solution, amino acids exist as dipolar ions (zwiterion) and this polar structure accounts for their high melting point (e.g. amino-ethanoic acid melts at 235^+C) solubility in water and insolubility in organic solvent.

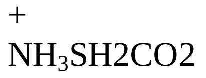
dipolar ion

Amino acids ads in three different fins depending as the pH of the medium



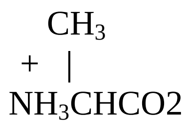
acid condition neutral condition basic condition

Examples of ten* no acids, with their amnion and IUPAC names; are given below.



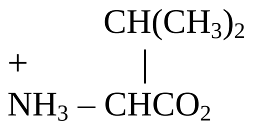
$$\overset{+}{N}H_3SH2CO2$$

2-amino ethanoic acid
(glycine)



$$\overset{+}{N}H_3\overset{CH_3}{\overset{|}{C}}HCO2$$

2-amino-propanoic acid
(alanine)



$$\overset{+}{N}H_3 - \overset{\overset{\displaystyle CH(CH_3)_2}{|}}{C}HCO_2$$

2-amino-3-methylbutanoic acid
(valine)

4.0 CONCLUSION

In this unit you have learned about fats and oils as naturally occurring alkalinities obtained from fatty acids and trihydric alkanols. You should have learned the varied sources of these classes of commands also known as lipids. Furthermore, you should have leaned how fats and oils can be converted into margarine and soap. You need to be awn of the various types of detagents and the advantages of soapless detergent ova soapy detergents. You were introduced to amino with and the polar nature of their structure.

5.0 SUMMARY

What you have learned in this unit concerns the source and uses of fats and oils. The unit also introduced you to the dipolar nature of amino acids and that they are the basic units of proteins. The unit that follows shall explain more about the chemistry of proteins.

6.0 TUTOR-MARKED ASSIGNMENTS

(a) explain the following
    (i) soap foamier") by saponification
    (ii) influence of pH ou the structure of amino acids
(b) Write briefly on detergents and their advantages over soap.
(c) Give the IUPAC name of the following
    i) $(CH_3)_2CHCH_2$ - $CH(NH_2)$ - $COOH$
    ii) $CH_3CH_2CH(CH_3)$ - $CH(NH_2)$ - $COOH$
    iii) State the relationship between the two structures

7.0 REFERENCES/FURTHER READING

Bajah, S.T Teibo B.O, Onwu G., aid Obikwere, A. (2002). *Senior Secondary Chemistry-Textbook* 3. Lagos. Longman Publishers.

Osei Yaw Ababio (2002). *New School Chemistry.* Onitsha Africa Fep Publishers.

UNIT 4 AN INTRODUCTION TO POLYMER CHEMISTRY

CONTENTS

1.0 INTRODUCTION

Polymers we very large molecules which are made up of repeating (recurring) structural units. Polymers are famed by the linking together of many smaller units (molecules) known as monomers, the overall process being known as polymerisation.

$$\underset{\text{monomer}}{nA} \rightarrow \underset{\text{polymer}}{A_n} \equiv -A-A-A-A-A-A-A-$$

Polymerisation is defined as the process (reaction) by which many simple molecules (monomers) join together to form giant molecules (polymers) of high molar mass (>200,000). That are two types of polymerisation, addition polymerisation and condensation polymerisation.

Some typical mammas and the corresponding polymer are listed below

Monomer	*polymer*
ahem	polythene
vinyl chloride	polyvinyl chloride
amino acids	proteins
glucose	starch

Polymers can be naturally-occuring e.g. protein, rubber, starch and cellulose, or synthesized in the laboratory e.g. polythene, nylon 66, polyvinyl chloride and terylene. The naturally occuring polymers are called natural polymers while the unmade polymers are called synthetic polymers.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define polymerisation
- distinguish between natural and synthetic polymers.
- real the different processes involved in polymerisation and the types of polymers obtains.
- recall different types of mammas and their corresponding polymers.
- list the uses of different types of polymers.

3.0 MAIN CONTENT

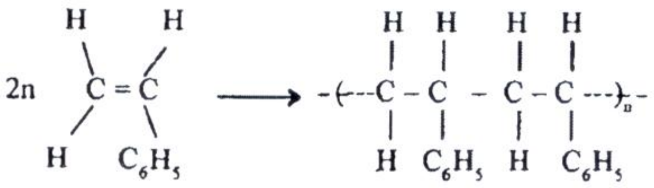
3.1 Polymerisation Processes

3.1.1 Addition polymerisation

Monomers which are unsaturated (having multiple bond) can react with each other to form addition compounds, a polymer with the same empirical formula as the monomer. Ethene and substituted edienes, for example, form addition polymer.

$$2n\ CH_2 = CH_2 \xrightarrow[high\ temp\ and\ pressure]{catalyst} -(CH_2 - CH_2 - CH_2 - CH_2)-_n$$

Ethane polythene



Phenylethene (styrene) poly(phenylethene) or polyrene

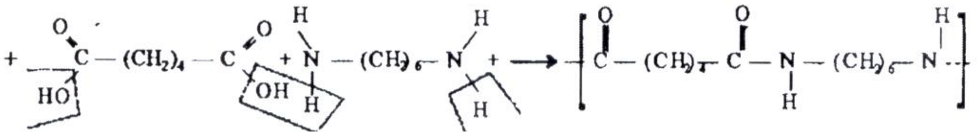
Several types of this polymer *and* their uses are listed in Table 14.1

TABLE 4.1

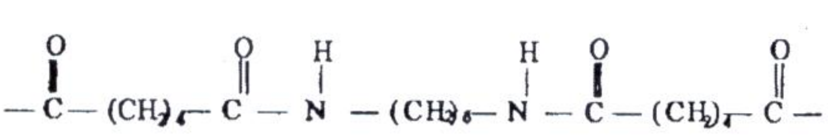
1.	Manager	Polymer	Common name	Uses
	$CH_2 = CH_2$ (ethane)	$[CH_2 - CH_2]_n$	Polyethene	Plastic bottles, pipes, toys and packaging material
2.	CH_2=CHCI (VINYL CHLORIDE)	$[CH_2 - CH_2]_n$	Polyvinyl Chloride (PVC)	Insulating material, pipe film, coatings and automobile parts
3.	CF_2=CF_2 (tetrafluoro-ethene)	$[CH_2 - CH_2]_n$	Poly (tetrafluoro-ethene) (Teflon)	High-temperature resistant rubber stopcocks, gaskets
4.	CH_2=CH($OCOCH_3$) (vinyl acetate)	$[CH_2 - CH_2]_n$ | $OCOCH_3$	Polyvinyl Acetate (PVA)	adhesives, emulsion pairs
5.	CH,=CHC_6H_5 (styrene)	$[CH_2 - CH]_n$ | C_6H_5	Polystyrene	Utensils, foam Toys and packaging

3.1.2 Condensation polymerisation

Condensation polymerisatiom maw between monomers that have at least two functional groups that can react or repeated with one another. The polymerisation process occur by the elimination of small molecules such as H_20 or NH_3 between two different monomer molecules each of which has at least two functional groups which can participate in the condensation. Nylon-6,6, for example, is a condensation polymer formed by the elimination of H_20 molecules from hexadioic (adipic) acid and hexane -1,6-diamine.



Nylon-6,6

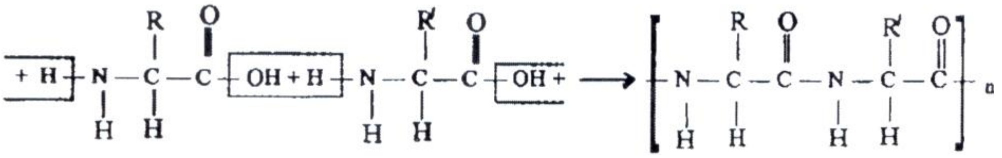


$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$$

Nylon-6,6

Nylon-6,6 is an example of a copolymer. When two different monomers, e.g. ethene and propene, hexadioic acid and hexane -1,6-diamine, react to give a polymer the product is called a co-polymer.

Another example of condensation polymerisation is the repeated condensation of amino acids with one another to give a protein molecule.



When the It and It are different then the protein molecule is a co-polymer.
Table 4.1 shows sane condensation polymers and their uses.

Table 4.1

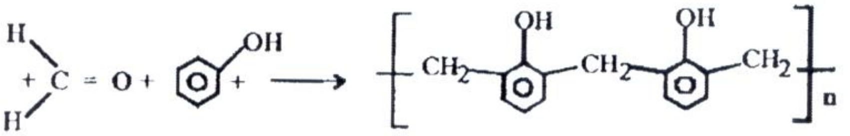
Monomer	*polymer*	*Uses*
1. hexamedioic acid + hrome-1.6-diamine	Nylon-6,6	Fabric, tiles, tyre cord
2. Benzene-1,4 dialkanoic acid +1,2-ethanediol	Terylene (polyester)	cloths, recording tapes. tyre cord.
3. amino acids	proteins	structural materials and biochemical functions for living organisms
4. glucose	starch (carbohydrate)	source of energy for living etyma

3.2 Plastics and Resins

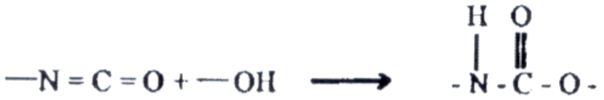
Plastics are high molar mass synthetic *(man-made)* polymers *that* can be defamed and molded into various shapes, at high temperatures. Linear polymers or copolymers have only weak van der waal's forces between their long chains These polymers and those with only a few, weak cross links between the chains are called thermoplastics because on heating they soften and on cooling harden again. Thermoplastics can be re-softened and re-hardened ova and ova again; and this hardly affects the property of the plastics. They are usually soluble in organic solvents.

Examples of thermoplastics are cellulose acetate, polythene, polyvinyl chloride. Thermoplastics are generally used in the form of molded shapes, fibres, pipe, sheets or films. They are generally very good insulators and are resistant to many chemicals. If the original thermoplastic is too brittle its properties can he changed by adding plasticisers e.g. esters of benzene dialkanoic Acids.

Polymers that contain highly cross-linked structure cannot be softened once they have hardened, that is they can only be heat-treated once. They are called thermosetting plastics and are insoluble in any kind of solvent. The rigidity in structure on cooling is as a result of chemical reactions leading to extensive cross-linking. Example of thermosetting plastics are phenol-methanal polyurethanes and alkyd resins.

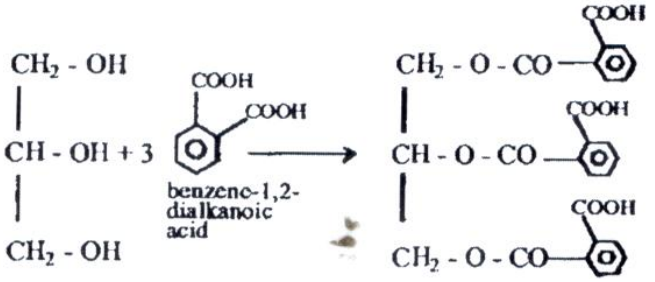


methanol phenol phenol-methanal polymer (Bakelite)



$$-N=C=O + -OH \longrightarrow -\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-$$

isocyanates from ends or triots urethane group



propane-1,2,3-triol alkyd resins

Thermosetting plastics are used to make articles such as electric plugs and switches, telephones, wireless and television cabinets, lavatory seats, at pays and plastic tableware. Bakelite is a good insulator^{-}, polyurethanes are used in floor finishes and bard-wearing paints, in the form of foams and alkyd resins are used as binding rains and in alkyd paints.

Naturally occurring resins are sticky substances, insoluble in water, that flows out from most plants when cut or secreted by plants and animals. Shellac is a natural *resin* oozes out by insects living on trees.

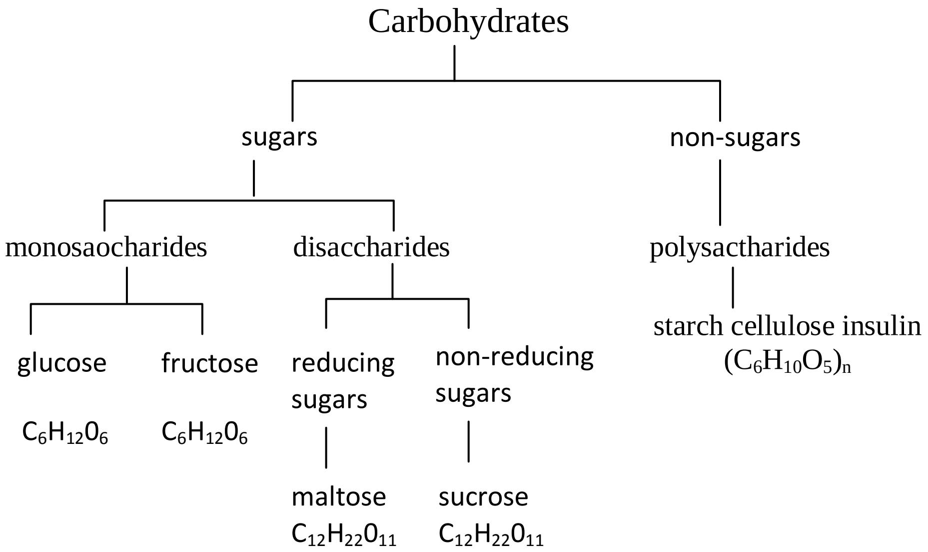
3.3 Natural Polymers

Polymer materials are widely found in living organisms where they play important Structural and physiological roles. Carbohydrates and proteins belong to this class of natural polymers.

3.3.1 Carbohydrates

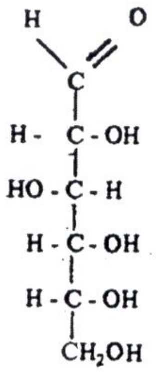
Carbohydrates *are* large groups °compounds with the molecular formula which can be written as ($C_x(H_2O)y$; such a formula does at, however, indicate the correct structural arrangement. All carbohydrates are composed of carbon, hydrogen and oxygen; among which includes sugars, starches and celluloses.

Carbohydrates can be classified as shown below

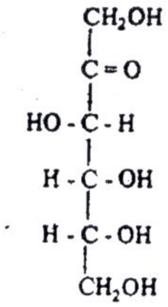


Sugars are crystalline substances with sweet taste and are soluble in water. They are generally classified into the monosaoccharides and the disaccharides. Non-sugars are complex molecules with relatively larger molar mass than the simple sugars.

(i) Monosaccharides: These are carbohydrates containing six or less carbon atoms pa molecule. Monosaccharides sugars cannot *be* hydrolysed into smaller sugar molecules, they *me* the simplest unit of carbohydrates. The two most important monosaccharide are glucose, which in an aldose oat (be……contains an aldehyde, -CHO group) and fructose, which is a ketoses (because it contains a keto, >C=0. group). They both have a molecular formula of $C_6H_{12}O_6$, but this represents many isomers.



Glucose



fructose

(ii) Disaccharides: These are carbohydrates containing twelve carbon atoms per molecule and having the molecular formula $C_{12}H_{22}0_{11}$. They are formed by the elimination of water molecule from two C_6 monosaccharide molecules i.e. $2C_6H_{12}0_6 – H_20 = C_{12}H_{22}O_{11}$. When hydrolysed, disaccharides split into two C_6 monosaccharides. There are two classes of disaccharides, the reducing sugars and the non-reducing sugars. A reducing sugar is a disaccharide, which turns Fehling's solution from blue to red; while a non-reducing sugar has no effect on Fehling's solution. Sucrose (a non-reducing sugar) and maltose (a reducing sugar) are the most important disaccharide.

Sucrose, which *is* obtained from sugar cane, is a colourless crystalline solid with a *sweet* taste. The *sugar which we* use for our tea is sucrose. On hydrolysis with dilute acids, sucrose gives equal amounts of glucose and fructose.

$$C_6H_{11}O_s - O - C_6H_{11}O_5 + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

sucrose glucose fructose

(iii) Polysaccharides: These are high molar mass polymers of monosaccharides. They are built up from many C_6 monosaccharides linked together in long-chains, with water molecule being eliminated between each pair of the C_6 molecules. Polysaccharides have a general formula

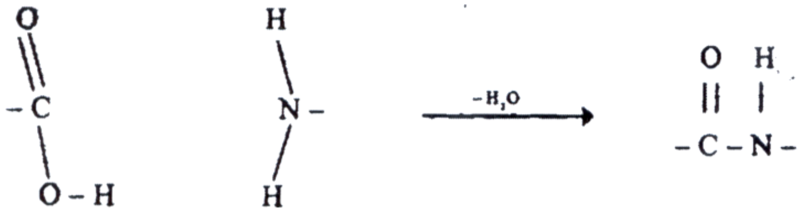
$$(C_6H_{10}0_5)_n \quad \text{i.e.} \ {}_nC_6H_{12}O_6 - H_20$$

where n=very large number

Important polysaccharides include starch ($n \approx 330$) and cellulose ($n \approx 600$). On hydrolysis, the polysaccharides split up into disaccharides and/or monosaccharides. Starch occurs as white granules in almost all plants e.g. rice, maize, barley, wheat and potatoes It is used hy plants as a reserve food supply and it provides a very important component of animal's diet as source of energy. Cellulose is the main constituent of the cell-walls of plants e.g. cotton, flax, jute, and is very widely distributed.

3.3.3 Protein

Protein is a group of complex polymers which occurs very widely in all planet-and inns. Typical examples of proteins are collagen (found in tissue and skin); keratin (found in hair, nails) and haemoglobin (oxygen carrier in blood). Proteins are made up of amino acids joined by what are knwn as peptide links. These are famed by the elimination of water molecule between the - COOH group of one acid and the -NH_2 group of an adjacent acid i.e.



from amino acids peptide link

Proteins we therefore polymers whose monomer is amino acids joined together by thy peptide link.

(a) Hydrolysis of proteins; Although different proteins vary widely in physical properties aid functions they can all be hydrolysed into a mixture of amino acids. The hydrolysis can be brought about by acids, alkalis or enzymes. About twenty different amino-acids have so far been isolated as product of protein hydrolysis. The protein, insulin, for example, yields sixteen different amino-acids. on hydrolysis

(b) Uses of proteins in living systems: Simple mains like collagen, is the structural material in connective tissue, skin and cartilage; keratin as a structural material in skin, hair and nails; insulin. as a hormone governing sugar metabolism; and haemoglobin as the oxygen carrier in blood. Some other proteins act as enzymes and as plant viruses.

3.4 Synthetic Polymers

Synthetic polymers are the man-made polymers, several of which has been mentioned in this unit. All the addition polymers hued in Table 4.1 are synthetic polymers. Several condensation polymers are also man-made, among which include polyesters (terylene) and polyamides (Nylon -6,6) - Table 4.2; synthetic rubber.

4.0 CONCLUSION

In this emit you have learned about polymers, as molecules made up of repeating structural¯min of Monomers You should have also learned that polymers can be natural or synthetic (man-made), all of which are made by either addition or condensation polymerisation process. You need to be aware of the importance of polymers to living organism and the device applications of polymers

5.0 SUMMARY

What you have learned in this unit concerns the sources, method of production; types and uses of natural and synthetic polymers. It has served to introduce you to this class of important compounds that is essential to us all

6.0 Tutor-Marked Assignments

i) Which of the following compounds can undergo addition polymerisation?
  a) Propene
  b) Hexane
  c) Benzene
  d) Butacliene

ii) List ten different polymers and give the name and structures of the monomers.

iii) Define the following tams with suitable statue' representation:
  a) Polymerisation
  b) Disaccharide
  c) Peptide link

7.0 REFERENCES/FURTHER READING

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002). *Senior Secondary Chemistry - Textbook* 3. Lagos: Longman Publishers.

UNIT 5 ENVIRONMENTAL IMPACT OF THE CHEMICAL INDUSTRY AIR AND WATER POLLUTION

CONTENTS

1.0 INTRODUCTION

You must have learned a lot about chemical facts and their relevance to living organisms. Chemistry has affected our life so much that we do not want to imagine life without it. The story of chemistry is not entirely a happy one mainly because people have of recent became aware of the effects of chemical processes in our environment. Of particular concern is the pollution of the environment caused by human activity and specifically those arising from the chemical industry.

Water and air are two essential elements of our physical environment because they sustain life. Similarly water and air are sources of essential raw materials for the chemical industry. Water as a universal solvent for numerous chemical process; for cooling and cleaning purpose; as well as for hydroelectric power generation. Some industrial raw materials such as salt, magnesium, calcium etc, are obtained from sea water. Air on the other hand, is the main source of oxygen and nitrogen. Oxygen is used as combustion fuel while nitrogen is used in the manufacture of ammonia, trioxonitrate (v) acid fertilizers, etc.

Ironically, the same water and air are the recipient of all industrial waters. Most of our wastes end up in the air or water. The chemical industry generates and discharges to much waste into the air and water that unless special care is taken the environment may be so polluted to the extent that our own lives could be in great danger. The quality of our air and water can deteriorate to the level that these essential elements of the environment may be sources of poison. This is the challenge currently facing our world in general and the chemical industry in particular.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- show the inter-relation between chemistry and the environment
- identify sources and effects of pollutants
- identify control measures for reducing the level of pollution
- explain the greenhouse effect and depletion of the ozone layer
- explain and identify biodegradable and non-biodegradable pollutants.

3.0 MAIN CONTENT

3.1 Water Pollution

Pure and drinkable water is normally an odourless, tasteless and colourless liquid. Water is used as a universal solvent for several purposes and discharged back into the environment.

- Can you imagine life without water?

The water used for any human activity is never returned the same, to its source. Used water contained dissolved or suspended foreign materials which are responsible for water pollution. The sources and nature of water pollutants are numerous but we shall discuss a few of them.

3.1.1 Phosphates

The detergent industry responsible for producing various cleaning agent is a large and essential industry. Everybody and all industries do one form of cleaning or the other, and only detergents have the characteristics for removing all types of stains. Phosphates are widely incorporated into detergents and hence are released in large quantities through water into rivers and lakes. Most fertilizers contain phosphates which are washed into rivers, lakes and underground water, when not utilized by plants.

Phosphates in rivers and lakes act as nutrients for the growth of algae and other water weeds. This reduces the oxygen level in the waters and prevent other living organisms in water e.g. fish from getting adequate supply of oxygen. The weeds also cover the surface of waters and hinder sufficient light, required for plant photosynthesis, from getting down the waters, and hence reduced food production.

3.1.2 Industrial discharges

Several industries dump their liquid and solid chemical *wastes* into rivers and streams. Depending on the type of industry; the chemical wastes may contain benzene, acetone, trichloromethane, retra-chloromethane, phenols, acids, alkalis etc. These chemicals constitute pollutants to water bodies and are hazardous to organisms that live in water and other living things that get in contact with such waters.

3.1.3 Pesticides

Increased food production *has* been achieved by the use of pesticides, which help control the damaging effects of pests to crops. Several of these pesticides e.g. DDT, which are toxic, end up in rivers and lakes. Mercury containing pesticides have been used over the years, and mercury which is toxic, easily concentrates in fish. When such fish is consumed, they can lead to mercury-poisoning.

3.1.4 Hot Water

Water is used as a coolant for machineries in several industries and the discharge of the hut water, which may seem harmless, can be source of pollution. Hot water raise the temperature of river water which may harm fish and also increase the growth of algae and other water weeds. The consequences of increased microbial growth in river water is as stated in Section 3.1.1

3.2 Air Pollution

Industrialization has caused an increase in the level of pollutants into the air and may be present in concentrations that can harm the environment and its inhabitants. The main cause of air pollution is the combustion of fossil filets such as coal, petrol and gases, by power plants and vehicles to obtain energy. The main air pollutants are discussed below.

3.2.1 Solid particles

Industrial processes such as coal burning, can lead to the emission of smoke, soot and dust which are discharged into the atmosphere. These pollutants when inhaled can damage the respiratory system particularly the lungs. Sometimes, the pollutants became trapped just above the earth's surface leading to the formation of smog, particularly over cities with high industrial emissions. Another toxic solid pollutant found in the atmosphere is lead emitted from the exhaust of motor vehicles using leaded petrol. Lead dust can cause lead poisoning and injury to the nervous system.

3.2.2 Oxides of carbon

Incomplete combustion of fuel lead to the formation of carbon (II) oxide (CO) which is a poisonous *gas*. With modernization and increase wealth, the *use* of motor vehicles has increased. Motor vehicles are the largest single source of carbon (II) oxide emission. When inhaled, carbon (II) oxide competes with oxygen for the haemoglobin in blood. This can lead to reduction in blood oxygen. Carbon (II) oxide gas causes dizziness, headaches, fatigue and can course death at high concentrations.

Carbon(iv) oxide (CO_2) is the principal product of the combustion of fossil fuel. The increase in the *use* of fossil fuels as source of energy has given rise to the excessive production of the *gas*. Plants use carbon(iv) oxide for photosynthesis The combined effect of deforestation and excessive combustion of fossil fuels has led to the increase in the level of atmospheric carbon (iv) oxide. The consequence of an increase in the level of carbon(iv) oxide is a greater retention of infrared ray in the earth, giving rise to the green house effect - a gradual warming of our planet. This occurrence will lead to the melting of the ice in the polar regions of the earth and many costal regions and islands on earth will then be submerged by the increase in ocean water level.

3.2.3 Oxides of Nitrogen and Sulphur

When sulphur-containing coal is burnt in electric power stations and industrial plants, sulphur(iv) oxide is produced This oxide of sulphur is acidic, corrosive and poisonous. Similarly, in the combustion of fuels at high temperatures, oxides of nitrogen e.g. NO and NO,, are produced.

The oxides of sulphur and nitrogen released into the atmosphere combine with rain-water to produce acids - the so-called acid rain. When acid rain falls it harms plant and animal life, building and metal structures. In addition, oxides of sulphur and nitrogen cause irritation of the eyes, nose, throat and respiratory tissues.

3.2.4 Hydrocarbons

Hydrocarbons such as methane, ethane, propane, butane, etc., which are constituents of fuels are released into the air through evaporation from storage tanks. These hydrocarbons are believed to cause cancer i.e. they are carcinogenic. The hydrocarbons are also known to react with oxides of nitrogen in the presence of lies to produce smog or heavily stagnant air, Hydrocarbons are known to retard the growth of plants and cause abnormal leaf and bud development.

3.2.5 Chlorofluorocarbons

Chlorofluorocarbons or CFCs are man-made chemicals e.g. freon, winch are used as propellants for spray cans like sheltox, coolants in refrigerators and air-conditioners, and for making plastic forms. When these chemicals are released into the atmosphere, ultra-violet light breaks off free chlorine atoms, CI, from the CFC molecule. The free chlorine atom which is very reactive, attacks a molecule of ozone, 0_3, to produce an ordinary oxygen molecule and other reactive species. The reaction is a chain reaction and the process is repeated numerous times. This causes a depletion or reduction in the ozone layer, which protects us on earth from harmful radiations released in the atmosphere.

The ozone layer is found in the stratosphere. Studies from satellites show a definite reduction in the ozone levels and revealed an 'ozone hole' (area without ozone protection) ova the Antartic. The effect of diminished ozone layer protection means an increase in the level of ultra-violet radiation that reaches earth. These radiations are known to cause cataracts (eye disease), skin cancer and sunburns.

3.3 Biodegradable and Non-Biodegradable Pollutants

The discharge of pollutants in the environment is an undesirable effect of industrial revolution. Many harmful chemical wastes from detergents, crude oil spill, insecticides and mercury compounds are non-biodegradable, i.e. they cannot be broken down into harmless compounds by living organisms They remain in the environment and harm its inhabitant For example, mercury accumulates in the body of aquatic organisms e.g. fish, which when eaten can eventually lead to mercury poisoning.

Some chemical pollutants are however biodegradable and are converted into harmless substances e.g. fertilizers by living organisms in the environment Sometimes harmful effluents are treated in sewage plants to convert them to useful chemicals utilizable for other purposes or before discharge into the environment.

3.4 Pollution Control

a) Legislations have been enacted in several countries to control the level of pollutant discharged into the air and water bodies. Agencies like FEPA have been established to monitor compliance with the legislations.
b) The use of unleaded petrol is encouraged to reduce emission of lead compounds.
c) Industrial effluents and emissions are treated to convert them to harmless biodegradable substances before being discharged.
d) The combustion of fuels are now more efficiently done, to reduce carbon(II) oxide emission, by proper tuning of and *the* use of catalytic converters in engines.
e) The emission of oxides of sulphur *can* be reduced by using sulphur-free crude oil or low-sulphur coal as fuel.
f) Aforestation programmes are now seriously encouraged in several countries.
g) The ban on the use of CFCs as refrigerants and propellants has been ratified by several countries
h) Education is an important anti-pollution measure, so that each of us is aware of the consequences of polluting our environment

4.0 CONCLUSION

In this unit you have learned a number of important issues that relate to the effects of the chemical industries in the environment. You should have learned about the sources and nature of *chemicals* that lead to pollution in water bodies and the air. Furthermore, you should have learned about the control measures aimed at reducing the level of pollution and saving our environment from danger.

5.0 SUMMARY

What you have learned in this unit concerns the effect of water and air pollution on our environment The pollution which is as a result of harmful substances, discharged from our chemical industries and combustion of fossil fuels, can cause serious harm to human, anima/ and plant life, and property. It has served to expose you to the hazards of industrialization and the control measures necessary to avert damage to our precious environment.

TUTOR0-MARKED ASSIGNMENTS

i) What are the main pollutants in
   a) air
   b) water?

ii) explain the green house effect and the depletion of the ozone layer.
iii) Enumerate six control measures aimed at reducing the level of pollution.

7.0 REFERENCES/FURTHER READING

Bajah, S.T., Teibo, B.O., Onwu, G. and Obikwere, A. (2002). *Senior Secondary Chemistry Textbook* 3. Lagos: Longman Publishers.

Osei Yaw Ababio.(2002). *New School Chemistry*. Onitsha: African-Fep Publishers.