Hydrocarbons

2.1 Organic compounds that consist of only Hydrogen (H) and Carbons (C) bonded to each other with a single bond or double bond or triple bond or a combination of all of them are know as Hydrocarbons. Hydrocarbons are divided into two major classes as shown in Fig (1)

![Hydrocarbons Diagram]

**Fig. 1** Classification of hydrocarbons
2.2 Alkanes

An alkane contains only carbon and hydrogen (a hydrocarbon) and contains only single bonds so that they termed as a saturated hydrocarbon. Alkanes have the general formula:

\[ C_nH_{2n+2} \]

That mean an alkane with 1 carbons \((n = 1)\) will have \(2(1) + 2 = 4\) hydrogen’s, and its molecular formula is CH\(_4\). An alkane with 2 carbons \((n = 2)\) will have \(2(2) + 2 = 6\) hydrogen’s, and its molecular formula is C\(_2\)H\(_6\) and so on.

<table>
<thead>
<tr>
<th>Name</th>
<th>molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
</tr>
<tr>
<td>Ethane</td>
<td>C(_2)H(_6)</td>
</tr>
<tr>
<td>Propane</td>
<td>C(_3)H(_8)</td>
</tr>
<tr>
<td>Butane</td>
<td>C(_4)H(_10)</td>
</tr>
<tr>
<td>Pentane</td>
<td>C(_5)H(_12)</td>
</tr>
<tr>
<td>Hexane</td>
<td>C(_6)H(_14)</td>
</tr>
<tr>
<td>Heptane</td>
<td>C(_7)H(_16)</td>
</tr>
<tr>
<td>Octane</td>
<td>C(_8)H(_18)</td>
</tr>
<tr>
<td>Nonane</td>
<td>C(_9)H(_20)</td>
</tr>
<tr>
<td>Decane</td>
<td>C(_{10})H(_22)</td>
</tr>
</tbody>
</table>

The simplest member of the acyclic saturated aliphatic alkane class is Methane. We will study this compound in more details as what we will learn about this simple compound can be applied on the big family to which it belongs i.e. the alkane family but of course with some modifications.
2.3. Structure of Methane CH$_4$

The structure of the methane molecule CH$_4$ is tetrahedral shape.

How this shape formed?

Methane has four C-H bonds formed as a result of overlapping between 1s orbital of an H atom with one of the sp$^3$ hybrid orbital to form a C-H bond. Four H atoms form four such bonds, and they are all equivalent. The CH$_4$ molecule is the most cited molecule to have a tetrahedral shape.

Let us see how these bonds formed.

The electronic configuration of the C is

\[ C^6 : 1s^2, 2s^22p^2 \]

Only two electrons but C forms 4 bonds so we need another two single electrons in order to be able to form 4 bonds to the carbon central atom. How that would happen?

The answer for the above question is the hybridization as one electron from the 2$s^2$ electrons has transferred to the empty p$_z$ orbital.
Now and after the promotion of one electron from the 2s orbital to the pz orbital we have 4 new orbital called sp. These orbitals have the same energy and the same shape. The energy of the new orbital is higher than the energy of the s orbital but lower than the energy of p orbital i.e. it is located in between the two energy levels.

Now because C forms 4 bonds it will use the 4 new hybrid orbital (1 from s and 3 from p) to form the 4 bonds it needs. We call this hybrid orbital sp³ because it formed by the combination between one s orbital and three p orbitals.

Now and before we represent the formation of the bonds in CH₄ using the atomic orbital we have to remember the shape of the orbitals.

- **s** orbital has a spherical shape.
- **p** orbital has a dumbbell-shaped. As you know we have three p orbitals pₓ, pᵧ, and pz that will lead to the following shape of p orbital.
sp hybrid orbital has dumbbell-shaped as well but with two different size of lobs that due to the overlapping between the s and p orbitals.

Now the CH₄ molecule is formed by the combination of sp³ orbital with 4 s orbital from 4 H atoms as the following

![Diagram of CH₄ molecule](image)

H-C-H bond is 109.5° tetrahedral shape

Always keep in your mind that:

1) When s orbital overlap with any of p orbital i.e. pₓ, pᵧ, pₗ from any side we obtain a bond called δ bond.

![Diagram of δ bond](image)

2) When s orbital overlaps with any of sp orbitals we obtain a δ bond.

![Diagram of δ bond](image)
3) When p orbital overlaps with another p orbital or another sp orbital there are two different possible Overlapping:

a) **Head to head overlapping** which produce δ bond as the overlapping is strong and the electrons are mix combine with each other in a good way that lead to formation of the strong δ bond.

![Diagram of p atomic orbital overlapping](image1)

b) **Side to side overlapping**

Side to side overlapping produce a different type of bonds known as π bond and we will consider it within the coming chapter.

![Diagram of p atomic orbital overlapping](image2)
How we can draw the structure of methane?

- Each dash represents two electrons i.e. one single bond.

- Each dot represents one electron. This structure shows the Lewis dot structure for the methane molecule.

The following structures show the actual shape of the methane, which is represented by simple 3D (three-dimensional) structure.

- Solid wedge shows a bond coming toward us i.e. out of the plane of the paper.
- Broken wedge shows a bond going away from us i.e. behind the plane of the paper.

3D structure of Methane
Physical Properties of Hydrocarbons (Methane)

Because carbon and hydrogen atoms have similar electronegativities (2.55 for C and 2.2 for H) there is very small charge polarization in the bond of hydrocarbons so that the polar interaction between hydrocarbons molecules is weak. Hydrocarbons are generally described as non-polar so that they are insoluble in polar solvents, such as water. However and although of the small polarization between C and H the methane itself is non-polar molecule because it has tetrahedral structure and the polarity of the individual C-H bonds cancel out each other. Methane has very low melting and boiling points m.p. -183 °C and b.p. -161.5 °C. When liquefied, Methane is less dense than water.

Tetrahedral structure of methane and the polarity of the individual C-H bonds cancel out each other

We use this arrow to indicate the polarity of a bond (dipole). The arrow goes from the less electronegative atom towards the higher one i.e. from positive to negative

Reactions of Methane

In general hydrocarbons are relatively chemical inert, this is due to the fact that hydrocarbons are non polar compounds. However; hydrocarbons undergo chemical reactions but at harsh and strong reaction conditions. We will look at the reactions of Methane as it represents a simple example for the reaction of saturated aliphatic hydrocarbons.
Oxidation (Combustion Reaction)

In a combustion reaction, a substance combines with oxygen (oxidation), releasing a large amount of energy in the form of heat. The energy released as heat by the complete combustion of one mole of a substance is called the heat of combustion. Carbon dioxide and water are the products of the complete combustion of hydrocarbons.

1) \[ \text{CH}_4 + 2\text{O}_2 \xrightarrow{\text{flame}} \text{CO}_2 + 2\text{H}_2\text{O} + \text{heat} \]
   this heat called heat of combustion and for methane its value is 213 Kcal

2) \[ \text{CH}_4 + \text{H}_2\text{O} \xrightarrow{850^\circ \text{C}} \text{Ni} \xrightarrow{} \text{CO} + 3\text{H}_2 \]

A substitution reaction (Chlorination)

A substitution reaction is a reaction in which one or more atoms replace another atom or group of atoms in a molecule. The reaction between methane and halogen gases, such as chlorine, to form an alkyl halide is an example of a substitution reaction. The methyl chloride CH\(_3\)Cl formed in the step 1 can undergo a further substitution reaction under the same reaction conditions to produce dichloromethane CH\(_2\)Cl\(_2\) or (methylene chloride) as in equation 2. Under the same reaction conditions CH\(_2\)Cl\(_2\) undergoes a further substitution to produce Chloroform CHCl\(_3\) as in equation 3 which produce carbon tetrachloride under the same reaction conditions as in step 4.

\[ \text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CH}_3\text{Cl} + \text{HCl} \] ..............1
\[ \text{CH}_3\text{Cl} + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CH}_2\text{Cl}_2 + \text{HCl} \] ..............2
\[ \text{CH}_2\text{Cl}_2 + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CHCl}_3 + \text{HCl} \] ..............3
\[ \text{CHCl}_3 + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CCl}_4 + \text{HCl} \] ..............4

Substitution reaction in methane can takes place 4 times
As you know chlorine Cl\textsubscript{2} is not the only halogen, there are another halogens which are Bromine Br\textsubscript{2}, Iodine I\textsubscript{2} and Fluorine F\textsubscript{2}. Do these halogens react with methane like the chlorine?

The direct and simple answer to this question is YES halogens other than Cl\textsubscript{2} react with methane to produce the halogenated products with one exception which is I\textsubscript{2}. Iodine does not react with methane CH\textsubscript{4} at all (actually it does react but the reaction is very slow to be significant). However the reaction of Br\textsubscript{2} and F\textsubscript{2} proceeds in different rates. In case of the Cl\textsubscript{2} the reaction is easy and producible, while in case of the Br\textsubscript{2} the reaction is less readily than in the case of Cl\textsubscript{2} but in the case of F\textsubscript{2} the reaction between CH\textsubscript{4} and F\textsubscript{2} is very vigorous reaction and it takes place even in the absent of light and heat i.e. it reacts at room temperature and at dark.

On the base of the above we can arrange the halogens in order of reactivity

\begin{align*}
\text{F}_2 & > \quad \text{Cl}_2 & > & \quad \text{Br}_2 & > & \quad \text{I}_2 \\
\text{very reactive} & & \text{reactive but less than F}_2 & & \text{reactive but less than Cl}_2 & & \text{very weak reactivity}
\end{align*}

This order of reactivity is applied not just on the reaction of methane but also for the hydrocarbons as well as most of the organic compound.

Now when we say for example that F\textsubscript{2} is more reactive than Cl\textsubscript{2} & Br\textsubscript{2} & I\textsubscript{2} we mean that F\textsubscript{2} reacts faster (the reaction rate) than the other halogens under the same reaction conditions i.e. the same temperature, the same concentration and the same other conditions. The series  F\textsubscript{2} > Cl\textsubscript{2} > Br\textsubscript{2} > I\textsubscript{2} called the \textit{relative reactivity} which means how a different reagents are reactive towards a particular compound to give a product.
**Reaction Mechanism:** the complete, step-by-step process of bond breaking and bond formation, leading to the observed product(s). It is a theoretical thing i.e. it is a proposed pathway to what happened during the chemical reaction.

**Mechanism of halogenations of Methane (Chlorination as example). Free Radical**

The halogenations (chlorination) of methane are believed to be proceeds *via* a free radical substitution. First we need to know what a radical or a free radical is?

We have seen before that a covalent bond is formed as a result of combination of two electrons from each single atom like the following:

![Formation of the covalent bond](image)

Now the covalent bond which formed as a result of sharing electrons between two species can be broken dawn in two deferent ways as the following:

![Types of breaking the covalent bond](image)
In the Heterolysis breaking of covalent bond both electrons from the bond that is broken goes to one fragment leading to formation of positive and negative charge (ions) on the two formed fragments (1).

Arrowheads with a complete head indicate heterolytic breaking of covalent bond

In the Homolytic breaking of covalent bonds each product gets one electron from the bond (2). The product of the hemolytic breaking of covalent bond is called radical or commonly uses term free radical.

Arrowheads with a “half” head (“fish-hook”) indicate homolytic breaking of covalent bond

What is a free radical?
It is a chemical species with a single unpaired electron, Its valence shell is one electron short of being complete so that radicals are very active species. Radicals are very active because they look for an electron in order to complete its valance electrons and achieve a stable situation.

Now let us go back to the mechanism of the chlorination of methane by \( \text{Cl}_2 \):

Steps in Radical Substitution

Three types of steps

- **Initiation step** – homolytic formation of two reactive species with unpaired electrons
  - Example – formation of Cl atoms from \( \text{Cl}_2 \) and light or heat.

- **Propagation step** – reaction with molecule to generate radical
  - Example - reaction of chlorine atom \( \text{Cl} \) with methane to give \( \text{HCl} \) and \( \text{CH}_3 \)·

- **Termination** – combination of two radicals to form a stable product:
  \[ \text{CH}_3· + \text{CH}_3· \rightarrow \text{CH}_3\text{CH}_3 \]

Now let us look at the mechanism in more details
The overall reaction is:

\[
\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CH}_3\text{Cl} + \text{HCl}
\]

Please note that in the absence of heat or light the reaction of Cl\(_2\) with CH\(_4\) will never happen. Very soon; we will know why?

The first step in the reaction mechanism is the **Homolytic** breaking of covalent bond between the Cl\(_2\) and this step will never takes place in dark and in the absence of light and or heat source as they are the major factor that causes the homolytic breaking of the bond and the generation of the free radical.

1) 
\[
\text{Cl-Cl} \xrightarrow{\text{heat or light at 250-400 } ^\circ\text{C}} 2\text{`Cl} 
\]

- Now the `Cl radical is very active and highly energetic. `Cl radical can break a bond in the methane molecule and abstract a partner `H with an electron (radical), giving substitution in the original molecule.
- After the `Cl abstract `H radical from the CH\(_4\) molecule; it forms another active radical called methyl radical `CH\(_3\) which is very active radical. The new formed `CH\(_3\) will attack the Cl\(_2\) molecule to abstract `Cl radical in order to achieve its stability as the following:

2) 
\[
\begin{align*}
\text{`Cl} + \text{H-CH}_3 & \rightarrow \text{`CH}_3 + \text{HCl} \\
\text{CH}_3 + \text{Cl-Cl} & \rightarrow \text{CH}_3\text{Cl}
\end{align*}
\]

The above two steps are called propagation steps. These two steps will not continue for ever but the reaction will stop finally at a step known as chain terminating step as the following:
In the chain terminating step no active partials (radicals) are generated but it is the step at which they are consumed. The consuming may take place in different ways as you can see in the above figure.

Now do you understand how the chlorination of methane takes place?

Please do not hesitate if you have any question.

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Higher Alkane than Methane CH₄

In the above discussion, we mainly focused on the Methane CH₄ and we said that is represents the alkane family in most of its reactions. Now let us look at a higher in carbon numbers alkane than CH₄ and let us learn some more new things.

\[ C_nH_{2n+2} \]

The above formula is general formula for Alkanes. That mean if \( n = 1 \) we will have CH₄ (methane). If \( n = 2 \) we have C₂H₆ (ethane). If \( n = 3 \) we will have C₃H₈ (propane) and so on. Return to page 2 to see the formula and names to the first 10 alkane.

We can draw the ethane molecule like any of the following form.
You have learned that the H atoms are connected to the C atom by $\delta$ bond, which is formed as a result of combination between the sp$^3$ hybridized orbitals on the C atom and the s orbital of the H, exactly as you have seen in the CH$_4$.

In the case of ethane C$_2$H$_6$ there is a bond between the two carbons C-C as you see in structure c.

**How the bond formed in the sense of orbitals and hybridization?**

Ethane molecule is symmetrical one i.e. if we break the bond between the C-C bond in C$_2$H$_6$ (just imagine we do so OK!)

![Ethane molecule](image)

Now we have each C atom bonded to 3 H atoms and we have seen that the bond between H and C are formed as a result of the combination between sp$^3$ on C and s of H as the following structure:

As you know C has 4 sp$^3$ hybridized orbital and it use 3 of them to make a bond with the H. How about the fourth sp$^3$ orbital?

The answer is it uses the fourth orbital to make a bond with the C to form the ethane C$_2$H$_6$ molecule. That mean the C-C bond in ethane is formed as a result of overlapping between two sp$^3$ orbital as the structure in the next page.
The above explanation leads us to the actual structure of Ethane \( \text{C}_2\text{H}_6 \) which is as the following:

**Conformation & Configuration**

In order to understand the difference between conformation and configuration let us look at the following two different compounds 1 and 2.

The molecule no 1 is and dimethyl ether as it has two methyl groups joined to each other via what we call ether bond (\( \text{CH}_3\text{OCH}_3 \)). The other molecule 2 is ethanol in which 2 carbons atoms are joined to each other and one of them is directly attached to OH group which we call it alcohol group.
These two molecules have the same molecular formula but they have completely two different structural formulas so they are two different compounds we called them before isomers.

Now if I gave you modules for the two molecules 1 and 2 and ask you to make ether from ethanol or vies versa you will never be able to convert from one structure to the other without breaking the bonds. In other words if you tried to rotate the bonds in 1 you will never get 2.

**Conformation & Configuration** [rotation or bond breaking]

Structures that can be interconverted ONLY by breaking one or more bonds have different configuration and are stereoisomers. [we will study this thing in the next chapter].

Structures that can be interconverted simply by rotation about C-C single bond are conformation of the same molecule.

Please note that the rotation can take place only in the single bonds (sigma bond) to go from one conformation to another. Molecules with single bonds can have so many
conformations as these conformations results from a free rotation about the single bonds due to the changes in energy.

Let us look at the ethane $\text{C}_2\text{H}_6$ and see how many different conformation it can adopt?

If you try to rotate the C-C bond in the ethane molecule you will get so many different conformations. However ethane has two extreme conformations (the most important two) they called \textbf{staggered} and \textbf{eclipsed} conformations, the large numbers of conformations between the staggered and eclipsed conformation called \textbf{skew} conformations.

\begin{itemize}
  \item \textbf{Staggered}
  \item \textbf{Eclipsed}
\end{itemize}

\textbf{How do we represent the staggered and eclipsed conformations?}

There are three different methods to represent the different conformations i.e. the staggered and eclipsed which are:

1) Andiron formula
2) Wedged & hashed lines formula
3) Newman projections formula

3) In the Andiron formula we represent the two different conformations as in the
following two figures. Please note that in the staggered conformation all the H atoms are far away from each others, while in the eclipsed conformation 2 of the H atoms are closed to each others.

2) Wedged & hashed lines formula
In the wedged & hashed lines formula atoms that project out of the plane of the paper are connected by a wedge and atoms that lie behind the plane of the paper are connected with a dashed wedge and atoms in the plane of the paper are connected by line —

3) Newman projections formula
We mainly will use the Newman projections formula as it is easy to use.

The Newman projections formula for staggered & eclipsed conformations
What are the circle and the dash mean?

Well, the ethane has two carbon atoms joining via δ bond. In the Newman projections the closed C atom and the 3 H atoms are represented by

The H atoms on the closed C atom

The C atom which is closed to you

The second C atom which is away from us is represented by circle

The H atoms on the far away C atom

The C atom which is far away from you

When you draw the eclipsed and staggered conformations please consider the following points:

2) The –H line must not pass the circle line like.

2) In the eclipsed conformation the two lines which represent the H atoms on the closed and the far away carbons must be exactly on each other, however we have to move them a little just to make the picture clear.

Wrong eclipsed and staggered conformations

What is the difference between the staggered & eclipsed conformations?
Well, you must know that the conformations have the same molecular formula, the same type of bond connectivity i.e. in two different conformations the atoms are bonded to same type of atoms but as you can see from the above structures that atoms are different in the arrangement of atoms in space so they are **stereoisomer**. We will study stereoisomer in the coming chapter. **However;** the different conformations for a molecule are arise as a result of the rotation about the C-C single bond. As a result of this rotation the molecules adapt different conformations which are mainly differ in **energy**. As the conformations has different energies they have different stability i.e. different conformations has different stability. The staggered conformation is more stable than the eclipsed conformation that mean the staggered has a less energy than the eclipsed conformation. The staggered conformation is lower in energy than the eclipsed by 3 k J mol\(^{-1}\). This is not much energy difference and the ethane molecule can get this energy at room temperature so the two conformations can be found but as we said before the ethane molecule stay in its staggered conformation most of the time as it is the most stable confirmation. The amount of energy required to rotate the ethane molecule (3 k J mol\(^{-1}\)) around C-C bond is called torsional energy. We say that eclipsed conformation is less stable than the staggered conformation because of the torsional strain.

**Why the staggered conformation is more stable than the eclipsed one or why its energy is lower than the energy of the eclipsed conformation?**

There are three important reasons to which the staggered conformation of ethane is more stable than the eclipsed conformation can be attributed.

1) The steric interaction between the atoms (H atoms in case of ethane) in the eclipsed conformation is big and it is reduced in the staggered conformation. However; the contribution of the steric factor in the case of ethane is small (about 10%) that because the H atoms are small in size to get in each other’s way. The steric factor effect becomes larger when higher alkanes are under study.

2) The electrons in the bonds repel each other and this repulsion is at a maximum in the eclipsed conformation.
From the above discussion we can conclude that the energy of the staggered conformation is lower than the energy of the eclipsed conformation and it is more stable, that as well means ethane molecules exist in the most stable staggered conformation.

**Conformations of propane CH₃CH₂CH₃**

When we study the conformation of propane, we can look in the same way as we were looking at the ethane molecule. In other word; propane is an ethane molecule in which a H atom in ethane is replaced by a CH₃ group as in the following figures.

Well, as a result of the replacing one H atom in ethane with CH₃ group, the propane is formed and now we have rotation around two carbon-carbon bonds not only one as it was in ethane. Again in the case of propane we have two different confirmations, the staggered and the eclipsed. As it was in the ethane; the staggered conformation is more stable than the eclipsed conformation. As a result of the change of small in size H atom with the larger in size CH₃ a little change in the rotational barrier is take place.
In the case of ethane it was \( (3 \text{ k J mol}^{-1}) \) but in case of propane it is \( (3.3 \text{ k J mol}^{-1}) \).

Now can you draw the staggered and the eclipsed conformations of propane?

It is exactly the same as the ethane but change one \( \text{H} \) in ethane with \( \text{CH}_3 \) to get the propane conformation.

**homologous series**

In chemistry, a homologous series is a series of organic compounds with a similar general formula, possessing similar chemical properties due to the presence of the same functional group, and shows a gradation in physical properties as a result of increase in molecular size and mass. Organic compounds in the same homologous series vary by a \( \text{CH}_2 \). For example, the alkane homologous series begins with methane (\( \text{CH}_4 \)), ethane (\( \text{C}_2\text{H}_6 \)), propane (\( \text{C}_3\text{H}_8 \)), butane (\( \text{C}_4\text{H}_{10} \)), and pentane (\( \text{C}_5\text{H}_{12} \)), each member differing from the previous one by a \( \text{CH}_2 \) group. From the definition we can write a general formula for members of the alkane homologous series which is

\[
\text{C}_n\text{H}_{2n+2}
\]

*If this is not clear please return to page 2 and page 17 or ask me and will be always happy to help you.*

**Nomenclature of Alkane**

The handout and exercises and homework of this section have been given out before. Remember that naming of organic compound in general needs to understand the IUPAC rules and then practice on the example given in the lecture, the text book and any other organic chemistry book or website.

If you have any question please do not hesitate to e-mail me, ask in the lecture and ask during the office hours.

**Classes of carbon atoms and hydrogen atoms**
Carbon atoms can be classified into four types depending on the number of carbons attached to the C atom under investigation. To understand this classification let us look at the following example and let us see the different classes of carbon and hydrogen atoms.

In the above example we call C number 1 as a **primary** carbon (1º) that because this carbon has only one bond to another C atom. In same time the H atoms that bonded to the primary C called a primary H’s. If the C atom bonded to two carbon atoms as in carbon number 2 we call it a **secondary** C (2º). Again the H’s attached to it are secondary hydrogen’s. In carbon number 3 as you see the C atom is bonded to another three carbon atoms so we call it a **tertiary** (3º) carbon atom and the only one H it has is called a tertiary hydrogen. Carbon number 4 has no hydrogen on it and it is bonded to other 4 carbon atoms so we call it a **quaternary** carbon atom.

### Hydrocarbons

#### Rules for Naming Hydrocarbons

In chapter 2 of your textbook, we covered the following classes of organic compounds: alkanes, halogenated hydrocarbons (including alkyl halides), cycloalkanes. This is intended to be a guide to naming these different types of compounds. Many of the rules of naming have been written differently than those in your textbook, and some rules have been expanded to be more useful.

**Alkanes –**

**IUPAC Rules of Naming:**

1. Saturated hydrocarbons are named according to the longest continuous chain (LCC) of carbon atoms in the molecule. Find the LCC in the compound and then assign a basic name that describes the number of carbons in the LCC (see Table 13.4 on page 335 of your textbook). This longest chain is the parent compound, and the suffix –*ane* indicates that the molecule is an alkane.

2. Number the LCC so that any substituents present have the lowest possible number. In the event that numbering the LCC from both directions gives the same locations, number the chain in the direction that give the first “point of difference”. If that doesn’t help, number the LCC in the direction that gives the lowest number to the substituent that comes first alphabetically.
3. Once the numbering has been figured out, note the names and locations of the attached substituents. Hyphens are used to separate numbers from names of substituents; commas separate numbers from each other.

4. Names of the substituent groups are placed in alphabetical order before the name of the parent compound. If the same substituent appears more than once, the position number of each substituent is noted. If the same group appears more than once on the same carbon, the position number is repeated as many times as the group appears. The number of identical groups is indicated by the Greek prefixes *di-* , *tri-* , *tetra-* , and so on (see Table 3.3 on page 79 of your textbook for a complete list up to 10). These prefixes are *not* used in determining the alphabetical order of the substituents. The last substituent to be named is “prefixed” to the name of the parent hydrocarbon, and is written as one word.

**Halogenated Hydrocarbons**

Rules for giving common names (for alkyl halides only):

1. Write the name of the alkyl group to which the halogen is attached. This is the first word in the common name.

2. Write the name of the halogen, with the ending changed to –ide (as in chloride, etc.) This is the second word in the common name.

*IUPAC Rules of Naming:*

- See the rules appropriate for the type of parent compound you have (i.e. alkane, aromatic, alkene, etc.)

- Use the proper stem for the substituent name (*fluoro-* for F, *chloro-* for Cl, *bromo-* for Br, and *iodo-* for I).

**Cycloalkanes**

IUPAC Rules of Naming:

1. Count the number of carbon atoms that make up the ring. Use this number to get the name of the parent hydrocarbon. Add the prefix *cyclo-* to the name of the parent hydrocarbon.

2. Note if there are any substituents on the ring. If there are, number the carbons in the ring to give the substituents the lowest possible numbers. If there is only one substituent, then no location is required, as it is understood that the substituent is attached to C-1.
3. When two or more substituents are present, list them in alphabetical order. Number the ring to give the lowest number to the substituent that comes first alphabetically.

4. If the substituent is an alkyl group that has more carbons than the ring itself, name the compound as a cycloalkyl-substituted alkane. For example

*Examples*

- 1,3-diethylcyclohexane
- 1-ethyl-1,3-dimethylcycloheptane
- 1-bromo-2-chloro-3-methylcyclobutane
- 1-ethyl-3-methyl-2-propylcyclopentane
- 1,1,2-trichlorocyclopropane
- 1,1-dimethyl-3propylcyclopentane
- 3-butyl-1,1-dimethyl-5-propylcyclohexane
- cyclodecane
- 1,3-diethyl-6-8-dimethycyclononane
- 1,2-dipropylcyclobutane
- 1,4-dimethyl-5-ethylcycloheptane
- 1-ethyl-2,3,3tripropylcyclobutane
- 4-ethylheptane
- 5-ethyl-5,6,6-trimethyldecane
- 4,5,6-trimethyl-5-ethyldecane
Hydrocarbons

3-ethyl-2,3-dimethylpentane
OR
3-methyl-3-isopropylpentane

2,4-dimethylheptane

4-ethyl-3-methyl-4,5-dipropyloctane

3-ethyl-3-methyl-4-propyloctane

4,5-diethyl-7-methyldecane

4-ethyl-5-propyloctane

2-bromohexane

2,4,5-trimethylheptane

1-iodo-5,6,6-trimethylheptane

2,3,4,5,6-pentamethyloctane

4-bromooctane

2,2,3-trimethylbutane

3-ethyl-2,2-dimethylpentane
Hydrocarbons

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**Reaction of Alkanes**

In general the reactions of alkane are limited. Alkanes can be described as hydrocarbons that do not have affinity for reactions. However, although of these general descriptions alkane still can make chemical reactions if suitable regents are used. In this section we will see what kind of chemical reaction alkanes can undergo. In page 8 we have talked in details about the reaction of the simplest alkane CH\(_4\) and we said that higher alkane can undergoes the same reaction as CH\(_4\) does, i.e. free radical substitution (halogenations) and oxidation. In this section we will see how the free radical substitution in higher alkane takes place. We will take Cl\(_2\) and Br\(_2\) as important examples for halogenations and we will make as well a comparison between these two halogen.

1) **Halogenations** (free radical substitution)

The same reaction conditions that applied in the case of halogenations of CH\(_4\) are used to make the free radical substitution on higher alkanes. Let us look at the following examples and see what the new things we will learn.

**Example 1**

\[ \text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CH}_3\text{Cl} + \text{HCl} \]

You have seen this reaction on page 13 and we have seen the mechanism of the reaction. Now if an alkane like ethane is reacted with Cl\(_2\) in the presences of light or heat what the product is?

**Example 2**

\[ \text{H} - \text{C} - \text{H} + \text{Cl}_2 \xrightarrow{\text{light} \ 25^\circ \text{C}} \text{H} - \text{C} - \text{Cl} \]

As you might expected the product is chloroethane. The Hs of the ethane molecule are all the same (identical) so any H can be substituted by the Cl atom.

**Example 3**

Now if propane is reacted with Cl\(_2\) under the same reaction conditions what are the products? Let us see

\[ \text{H} - \text{C} - \text{H} + \text{Cl}_2 \xrightarrow{\text{light} \ 25^\circ \text{C}} \]

1. \[ \text{H} - \text{C} - \text{C} - \text{Cl} \] (45%)
2. \[ \text{H} - \text{C} - \text{C} - \text{H} \] (55%)
In the case of propane we obtained a mixture of two products which are 1-chloropropane and 2-chloropropane in 45% and 55% yield respectively.

Well, we have a mixture of two products 1 and 2 because we have two different types of carbon and hydrogen as you see in the following figure.

Because of the two different types of Hs presents in propane the Cl can substitute over any H of the two different types producing two different products which are isomers. Remember isomers are different compound have the same molecular formula but them differing in the orientation in the space.

But why we have about 45% and 55% yield of 1-chloropropane and 2-chloropropane respectively?

Let us see some more examples and then we will answer this question?

**Example 4**

When n-Butane undergoes hydrogenation with Cl₂ it gives a mixture of two isomers 1-chlorobutane and 2-chlorobutane in 28% and 68% yield respectively. Again it gives a mixture of two isomers 3 and 4 because there are two different types of Hs so Cl can substitute over any H of the two different types producing two different products exactly as in the case of propane, but in butane the ratio between the two product is higher than the ratio between the two formed products in case of propane? Why let us see the last example before we answer all the above questions we have asked our self.
**Example 5**

The reaction of Isobutane with Cl\(_2\) under the same reaction condition gives a mixture of two isomers exactly as what happened in all of the previous examples. The two isomers 1-chloro-2-methylpropane and 2-chloro-2-methylpropane are formed in 64% and 36% yields respectively. Again we have a mixture of isomers because we have two different types of Hs at which the Cl can substitute over.

*Now you know that we always have a mixture of isomers in the free radical substitution on alkane because we have different types of hydrogen's.*

Now we will learn why we have different percentage yields for the mixture of the isomers formed? And why none of the isomers is predominate?

There are two reasons for this out come. The first reason is due back to the reactivity of Cl\(_2\) comparing to the reactivity of the Br\(_2\). Cl\(_2\) is more reactive than the Br\(_2\) so it hit the H in the alkane indiscriminately that mean its not selective, while Br\(_2\) is less reactive and it chose the best position to attach. We mean by the best position here in the content of 1\(^0\), 2\(^0\) or 3\(^0\) positions. From this discussion we need to learn a general roll which is law reactivity give high selectivity and *vies versa.*