South valley University

Faculty of Education

Principles of Organic Chemistry

1st year students

Chemistry Group

First term 2023/2024

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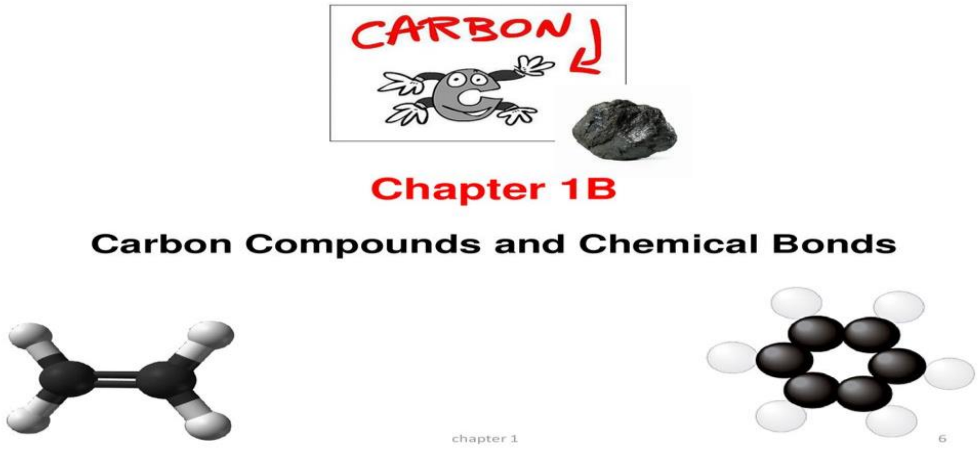

Chapter 1B

Carbon Compounds and Chemical Bonds

chapter 1

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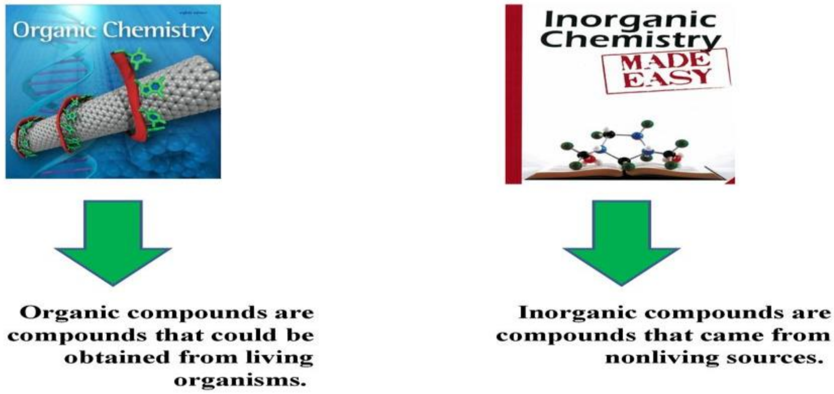
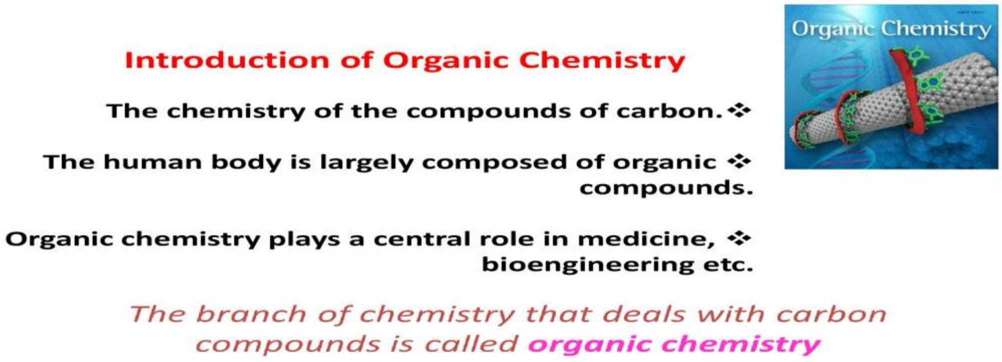


Organic compounds are compounds that could be obtained from living organisms.

Inorganic compounds are compounds that came from nonliving sources.

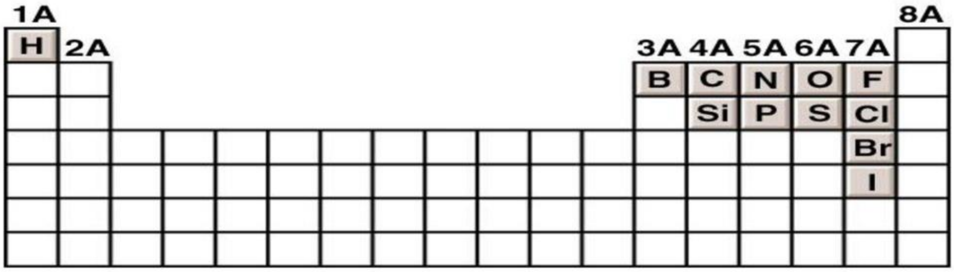


Introduction of Organic Chemistry

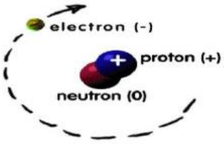
- **The chemistry of the compounds of carbon.**
- **The human body is largely composed of organic compounds.**
- **Organic chemistry plays a central role in medicine, bioengineering etc.**

*The branch of chemistry that deals with carbon compounds is called **organic chemistry***

Common Elements in Organic Compounds

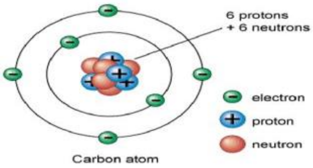


The structure of atom



Simplified structure of an atom

structure of carbon atom



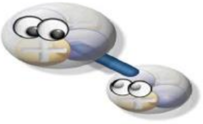
Chemical Bonds: The Octet Rule

Octet Rule

- Atoms form bonds to produce the electron configuration of a noble gas (because the electronic configuration of noble gases is particularly stable).
- For most atoms of interest this means achieving a valence shell configuration of 8 electrons corresponding to that of the nearest noble gas.
- Atoms close to helium achieve a valence shell configuration of 2 electrons.
- Atoms can form either ionic or covalent bonds to satisfy the octet rule.

G. N. LEWIS

Chemical Bonds



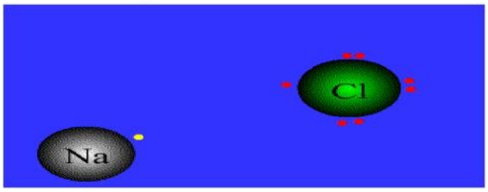
A chemical bond is a force of attraction that holds two atoms together to fill its electron shells with 8 electrons (octet rule).

Kinds of chemical bonds:

1. Ionic bonds
2. Covalent bonds
3. Metallic bonds

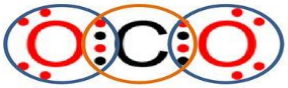
IONIC BOND

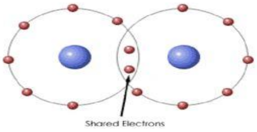
bond formed between two ions by the *transfer* of electrons

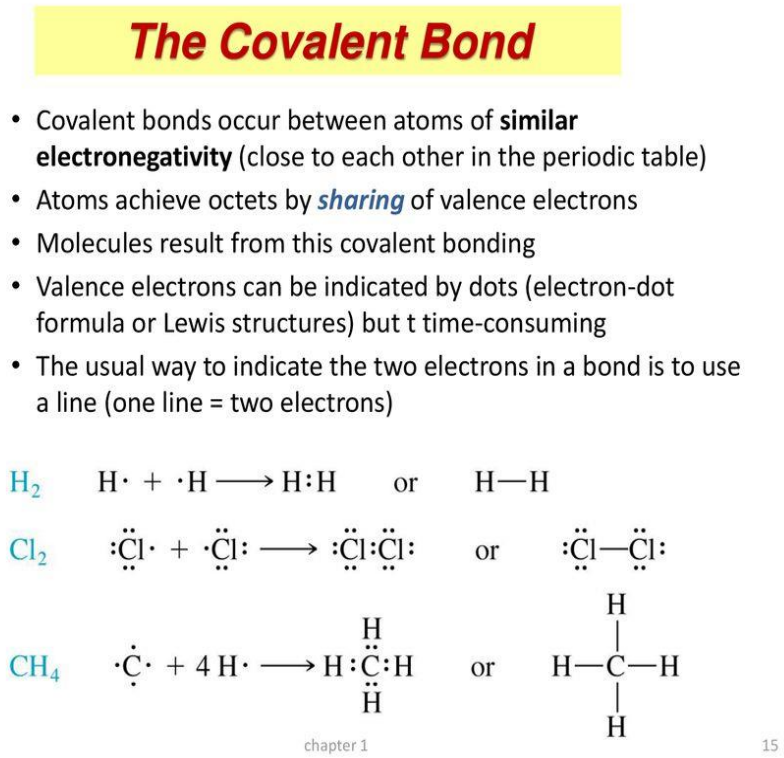


The Covalent Bond

A ***covalent bond*** is a chemical bond formed between (nonmetal + nonmetal) or (metalloide + nonmetal) in which two or more electrons are shared by two atoms.







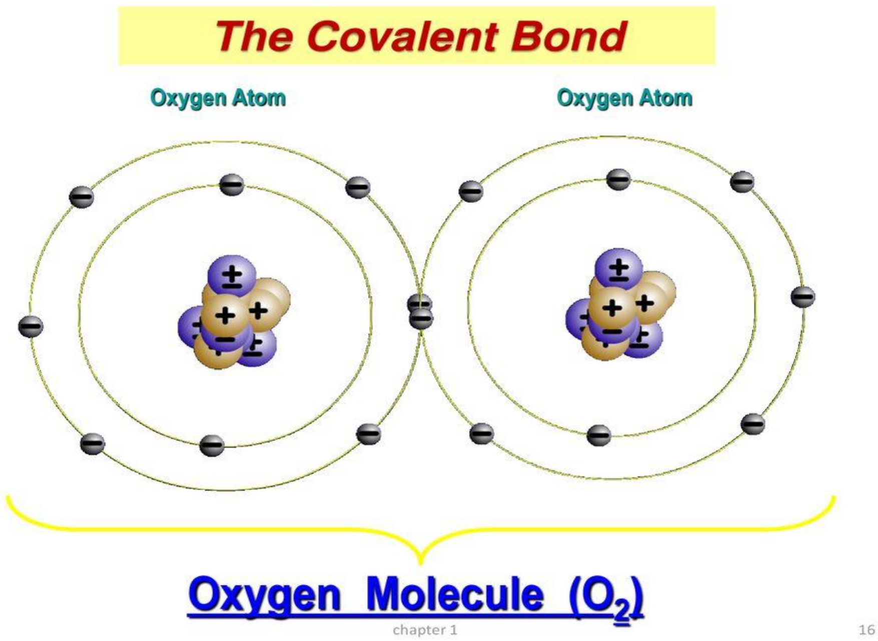
The Covalent Bond

- Covalent bonds occur between atoms of **similar electronegativity** (close to each other in the periodic table)
- Atoms achieve octets by ***sharing*** of valence electrons
- Molecules result from this covalent bonding
- Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but t time-consuming
- The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)

H_2 $\quad H\cdot + \cdot H \longrightarrow H{:}H \quad \text{or} \quad H{-}H$

Cl_2 $\quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \longrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \quad \text{or} \quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$

CH_4 $\quad \cdot\underset{\cdot}{\overset{\cdot}{C}}\cdot + 4\,H\cdot \longrightarrow H{:}\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}{:}H \quad \text{or} \quad H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H$



The Covalent Bond

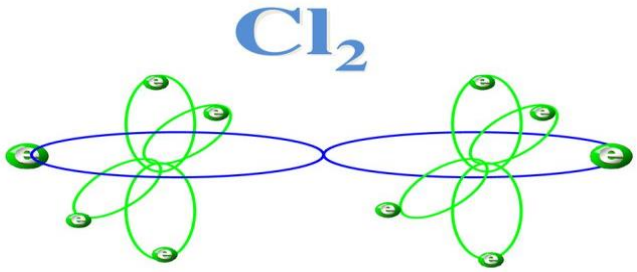
Oxygen Atom

Oxygen Atom

Oxygen Molecule (O_2)

The Covalent Bond

The sharing of a pair of electrons between 2 atoms.



– Covalent Bonds

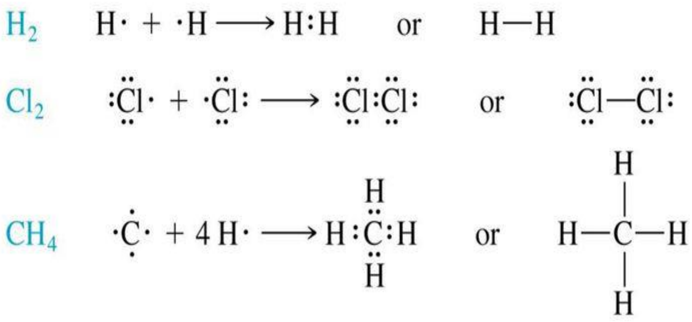
– Non polar covalent Bond

è Atoms achieve octets by *sharing* of valence electrons

è Molecules result from this covalent bonding

è Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but this is time-consuming

è The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)



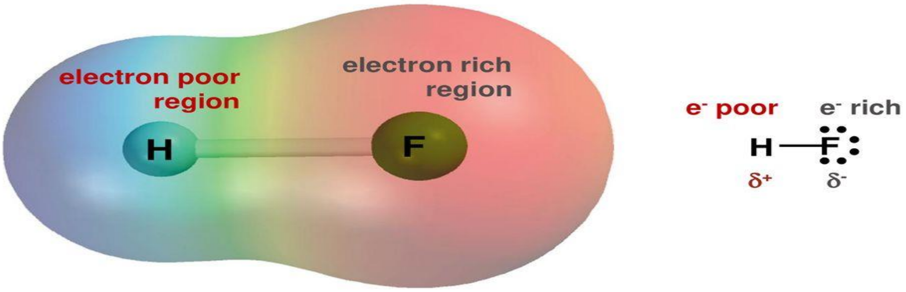
$$H_2 \quad H\cdot + \cdot H \longrightarrow H{:}H \quad \text{or} \quad H{-}H$$

$$Cl_2 \quad :\ddot{\underset{..}{Cl}}\cdot + \cdot\ddot{\underset{..}{Cl}}: \longrightarrow :\ddot{\underset{..}{Cl}}{:}\ddot{\underset{..}{Cl}}: \quad \text{or} \quad :\ddot{\underset{..}{Cl}}{-}\ddot{\underset{..}{Cl}}:$$

$$CH_4 \quad \cdot\dot{\underset{\cdot}{C}}\cdot + 4\,H\cdot \longrightarrow H{:}\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}{:}H \quad \text{or} \quad H{-}\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}{-}H$$

2-Polar covalent bond or polar bond

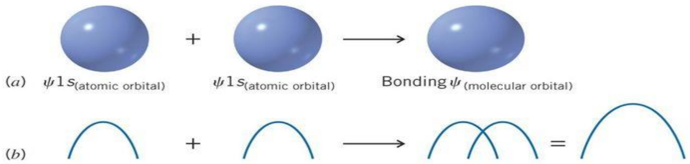
is a covalent bond with greater electron density around one of the two atoms



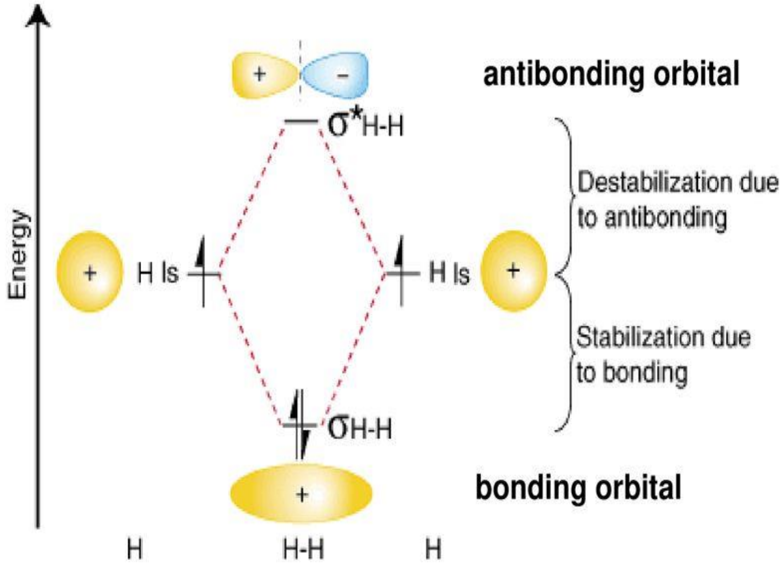
- **Orbital**: a region in space where the probability of finding an electron is large
- **Atomic Orbitals (AOs):** The region of space where one or two electrons of an isolated atom are likely to be found.
- **Molecular Orbitals (MOs)** :The region of space where one or two electrons of a molecule are likely to be found.

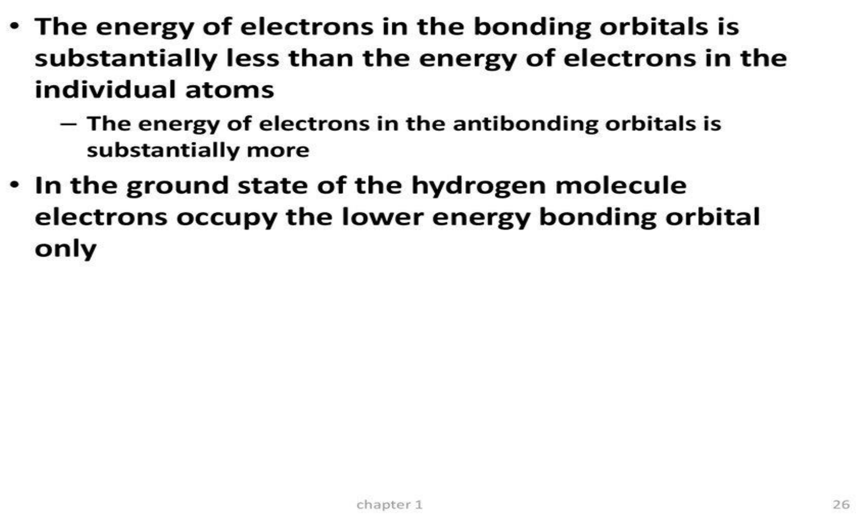
– Bonding Molecular Orbitals (Ψ_{molec})

- **AOs combine by addition (the AOs of the same phase sign overlap)**
- **The value of Ψ^2 (electron probability density) in the region between the two nuclei increases**
- **The two electrons between the nuclei serve to attract the nuclei towards each other**
- **This is the ground state (lowest energy state) of the MO**

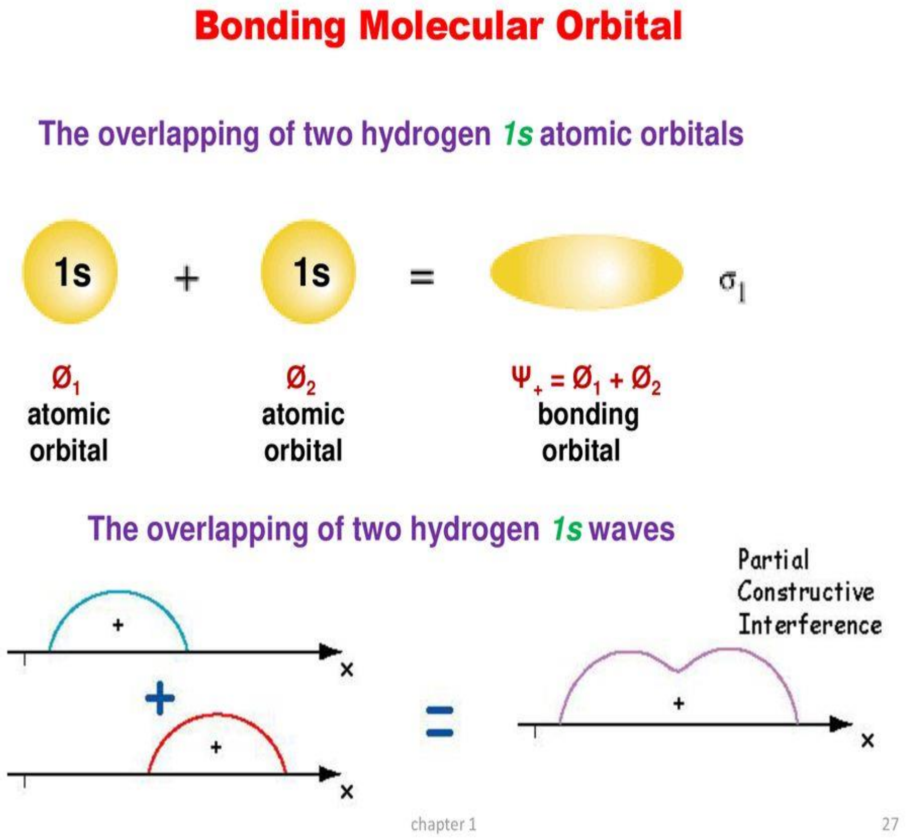


Molecular Orbital of Hydrogen





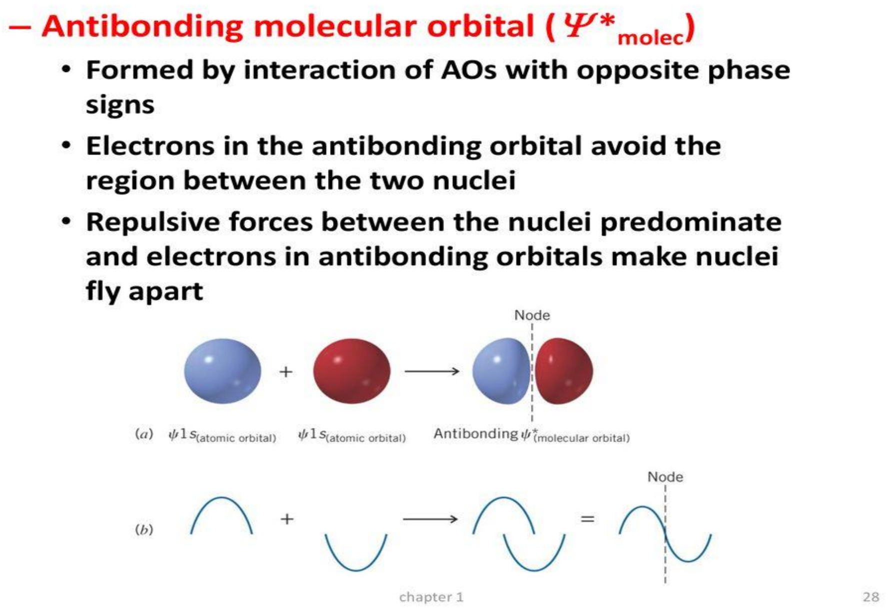
- **The energy of electrons in the bonding orbitals is substantially less than the energy of electrons in the individual atoms**
  - **The energy of electrons in the antibonding orbitals is substantially more**
- **In the ground state of the hydrogen molecule electrons occupy the lower energy bonding orbital only**



Bonding Molecular Orbital

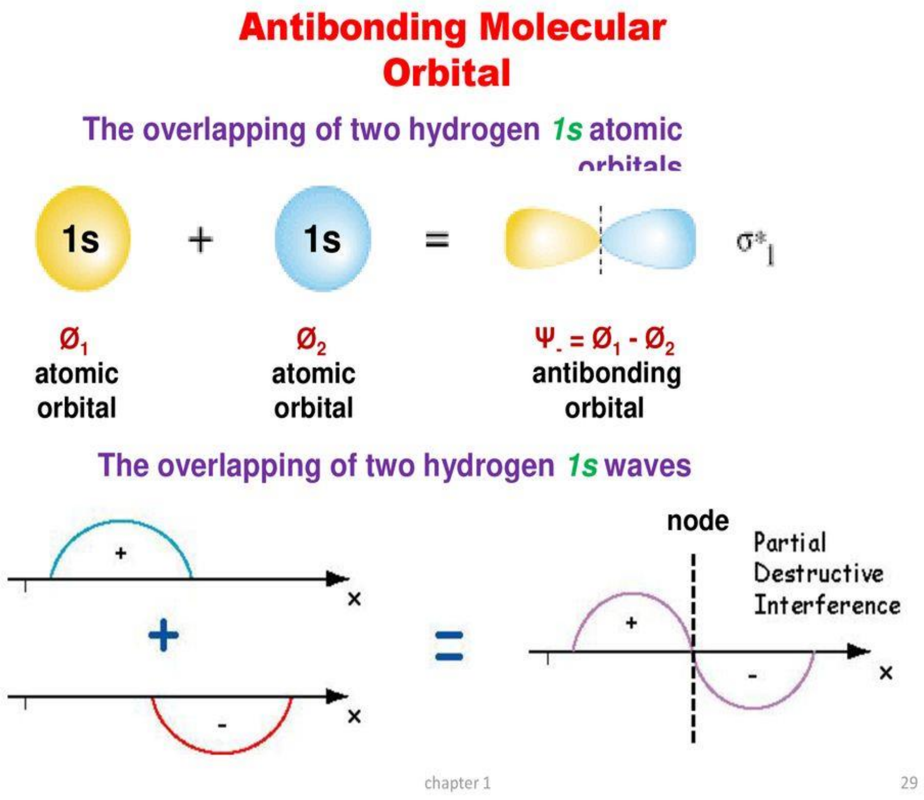
The overlapping of two hydrogen *1s* atomic orbitals

The overlapping of two hydrogen *1s* waves



– Antibonding molecular orbital (Ψ^*_{molec})

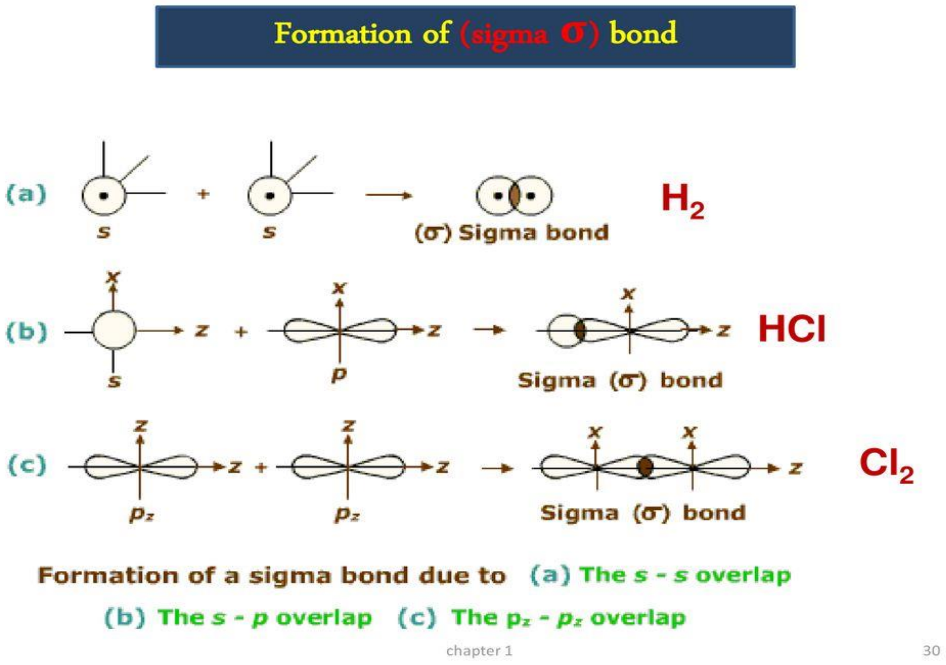
- **Formed by interaction of AOs with opposite phase signs**
- **Electrons in the antibonding orbital avoid the region between the two nuclei**
- **Repulsive forces between the nuclei predominate and electrons in antibonding orbitals make nuclei fly apart**



Antibonding Molecular Orbital

The overlapping of two hydrogen *1s* atomic orbitals

The overlapping of two hydrogen *1s* waves



Formation of (sigma σ) bond

Formation of a sigma bond due to (a) The *s* - *s* overlap (b) The *s* - *p* overlap (c) The p_z - p_z overlap

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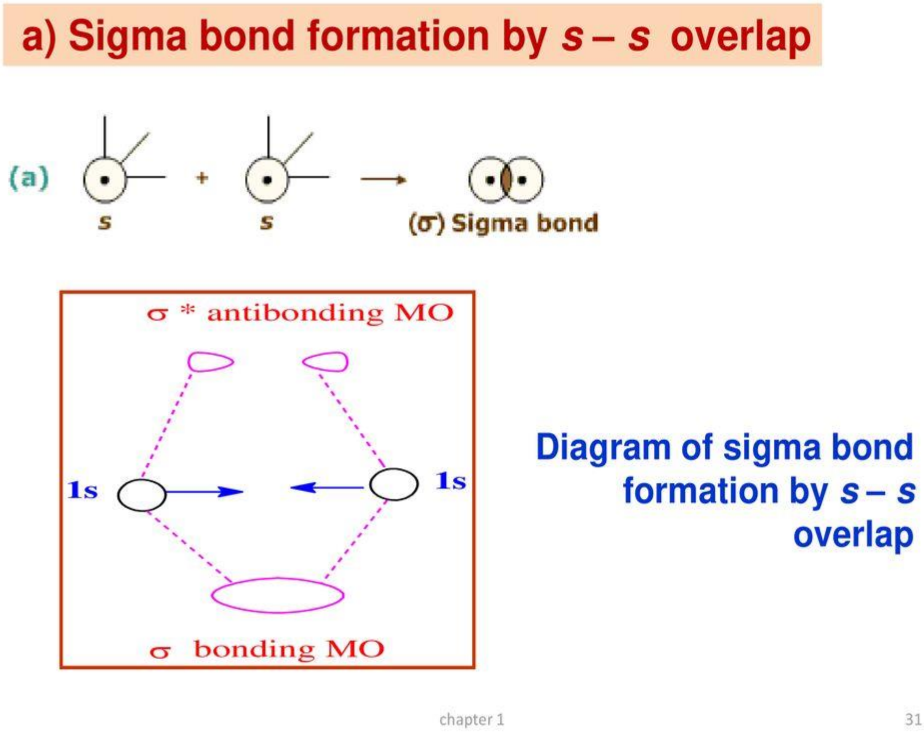

a) Sigma bond formation by *s* – *s* overlap

Diagram of sigma bond formation by *s* – *s* overlap

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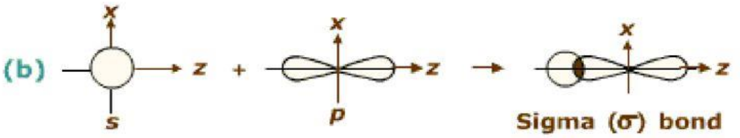
b) Sigma bond formation by *s* – *p* overlap



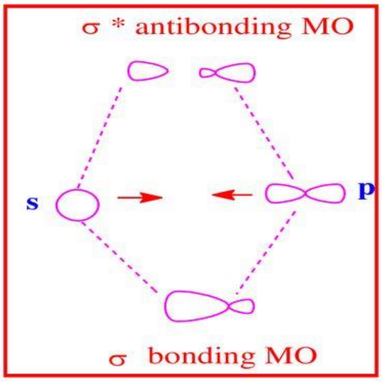
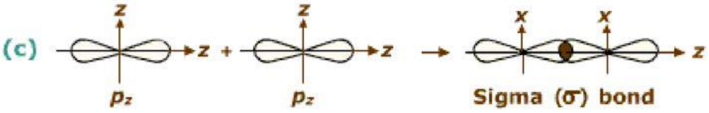


Diagram of sigma bond formation by *s* – *p* overlap

c) Sigma bond formation by *p* – *p* overlap



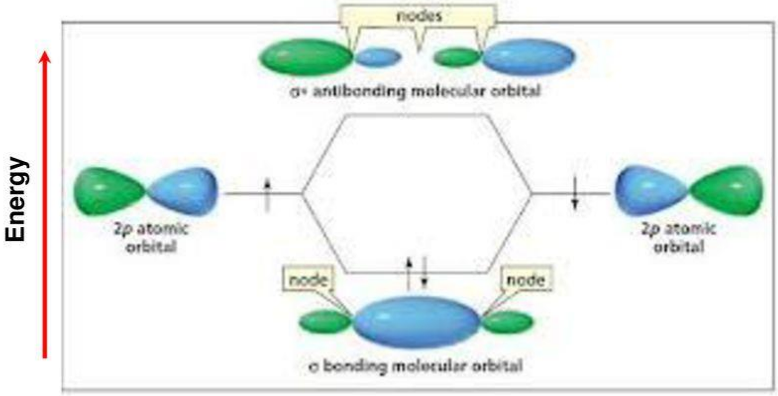
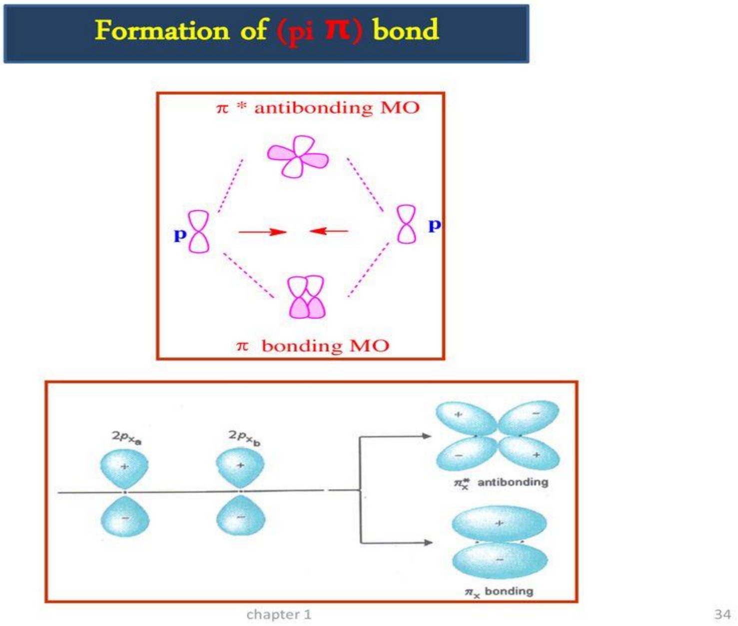
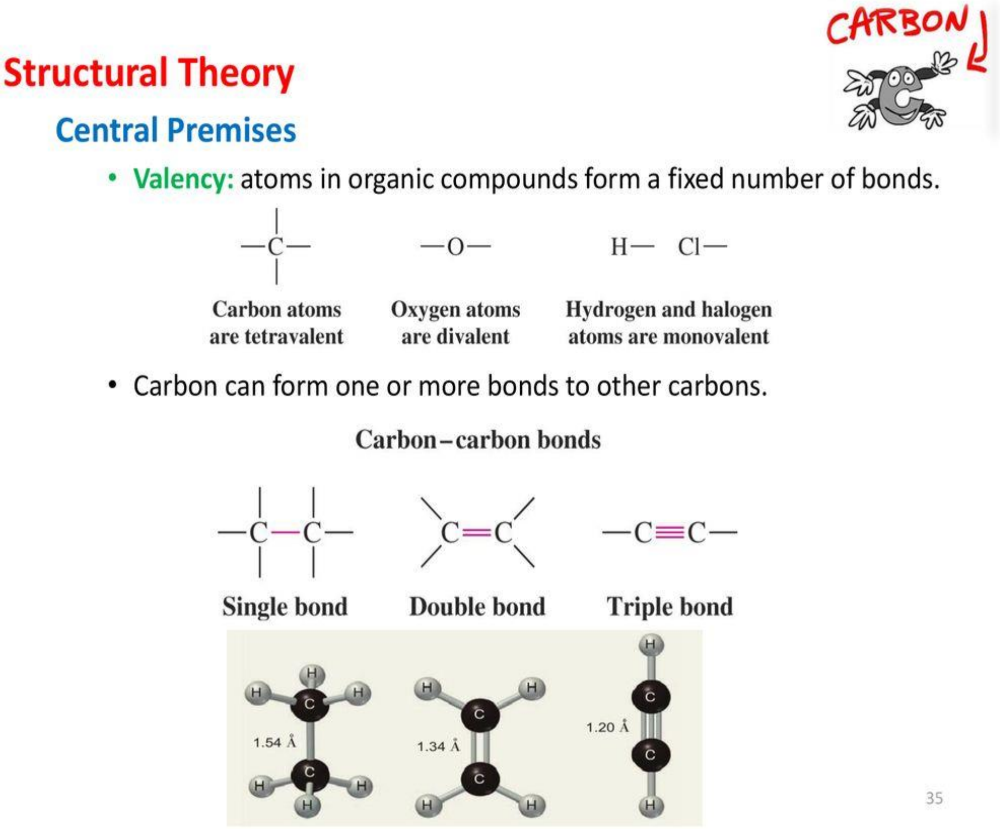


Diagram of sigma bond formation by *p* – *p* overlap



Formation of (pi π) bond



Structural Theory

Central Premises

- **Valency:** atoms in organic compounds form a fixed number of bonds.

Carbon atoms are tetravalent

Oxygen atoms are divalent

Hydrogen and halogen atoms are monovalent

- Carbon can form one or more bonds to other carbons.

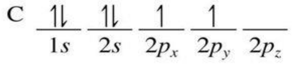
Carbon–carbon bonds

Single bond

Double bond

Triple bond

- **The Structure of Methane and Ethane: sp^3 Hybridization**
  - **The structure of methane with its four identical tetrahedral bonds cannot be adequately explained using the electronic configuration of carbon**



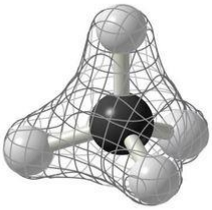
Ground state of a carbon atom

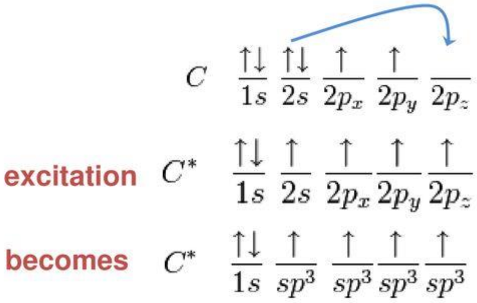
  - **Hybridization of the valence orbitals (2*s* and 2*p*) provides four new identical orbitals which can be used for the bonding in methane**
  - ***Orbital hybridization* is a mathematical combination of the 2*s* and 2*p* wave functions to obtain wave functions for the new orbitals**

- **When one 2*s* orbital and three 2*p* orbitals are hybridized four new and identical sp^3 orbitals are obtained**
  - When four orbitals are hybridized, four orbitals must result
  - Each new orbital has one part *s* character and 3 parts *p* character
  - The four identical orbitals are oriented in a tetrahedral arrangements
  - The antibonding orbitals are not derived in the following diagram

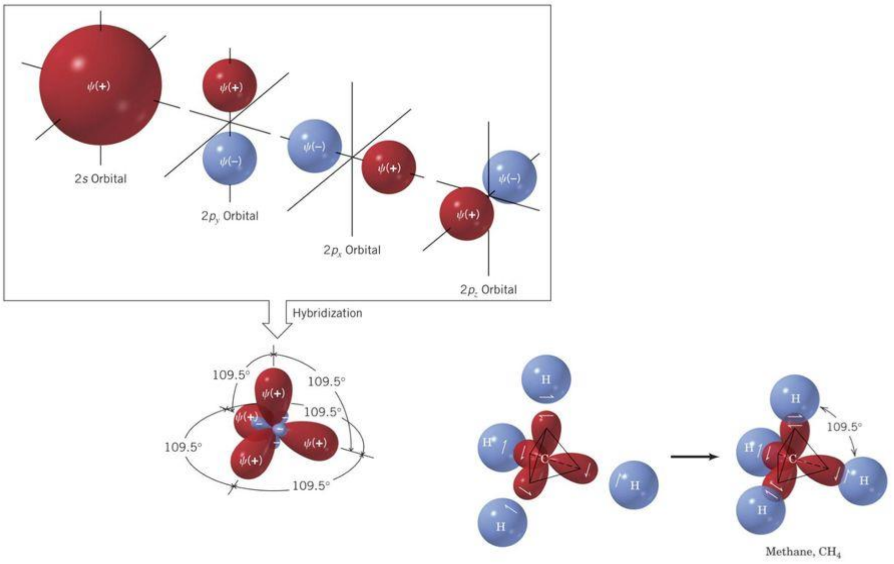
- **The four sp^3 orbitals are then combined with the 1*s* orbitals of four hydrogens to give the molecular orbitals of methane**
- **Each new molecular orbital can accommodate 2 electrons**

sp^3 hybridization in Methane CH_4

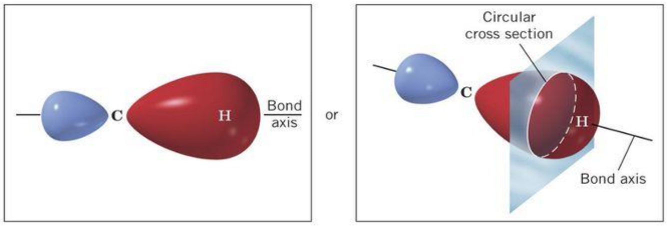


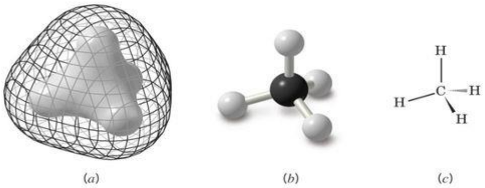


Ground state **excited state**



Methane, CH_4





- **A variety of representations of methane show its tetrahedral nature and electron distribution**
  - a. calculated electron density surface b. ball-and-stick model c. a typical 3-dimensional drawing

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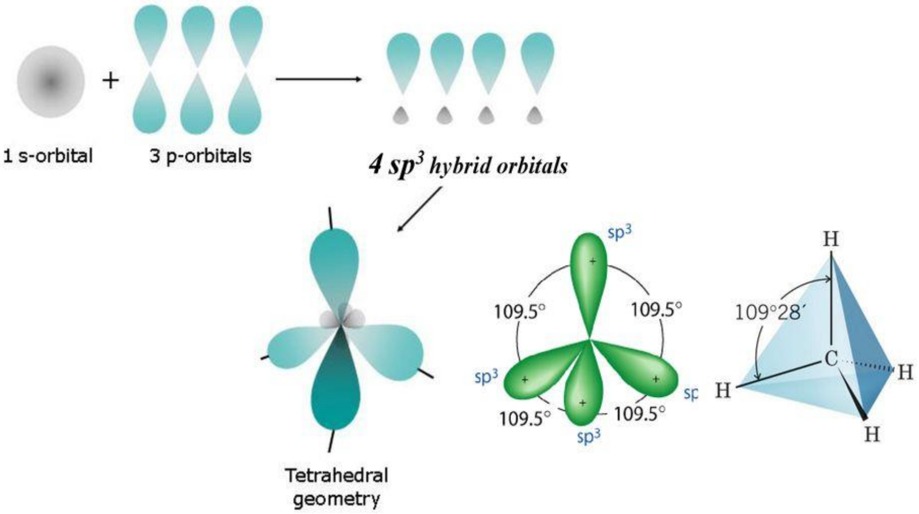
Molecule geometry of CH_4



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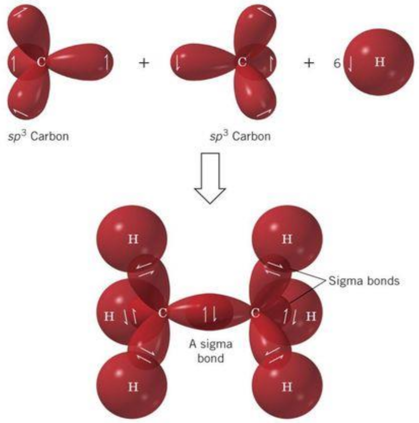
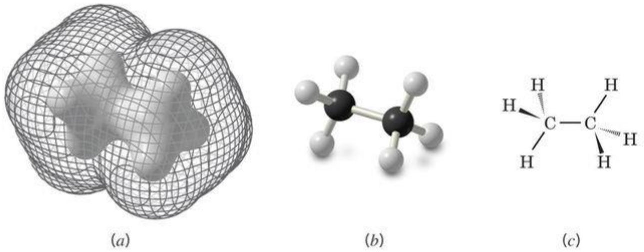
– Ethane (C_2H_6)

- **The carbon-carbon bond is made from overlap of two *sp³* orbitals to form a σ bond**
- **The molecule is approximately tetrahedral around each carbon**



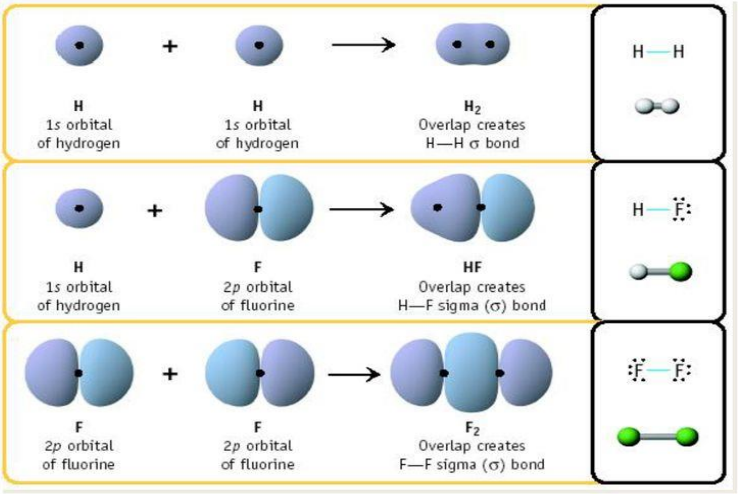
- **The representations of ethane show the tetrahedral arrangement around each carbon**
  - a. calculated electron density surface b. ball-and-stick model c. typical 3-dimensional drawing



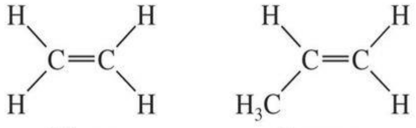
Generally there is relatively free rotation about σ bonds

- Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane

Examples of Sigma Bond Formation

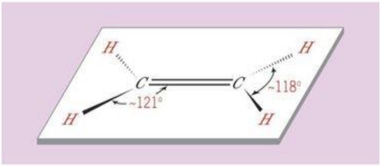


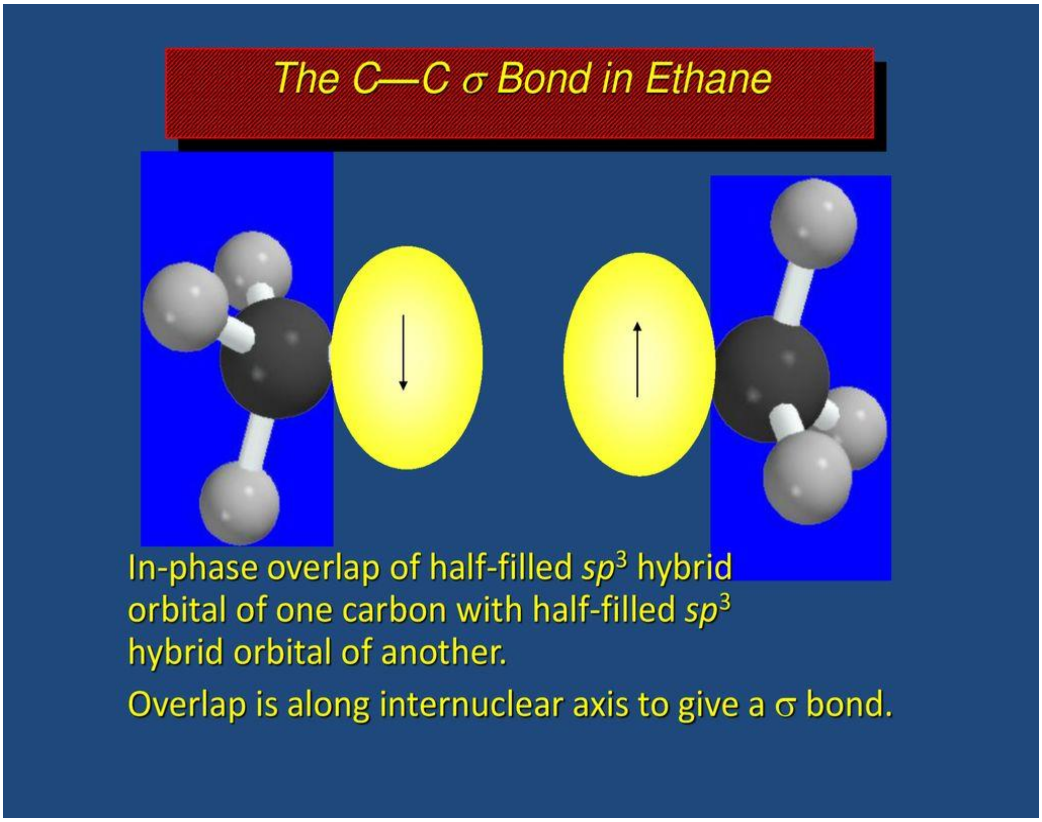
- **The Structure of Ethene (Ethylene) : *sp*^{2} Hybridization**
  - **Ethene (C_2H_2) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes***
    - **Another example of the alkenes is propene**



Ethene **Propene**

  - **The geometry around each carbon is called *trigonal planar***
    - **All atoms directly connected to each carbon are in a plane**
    - **The bonds point towards the corners of a regular triangle**
    - **The bond angle are approximately 120°**

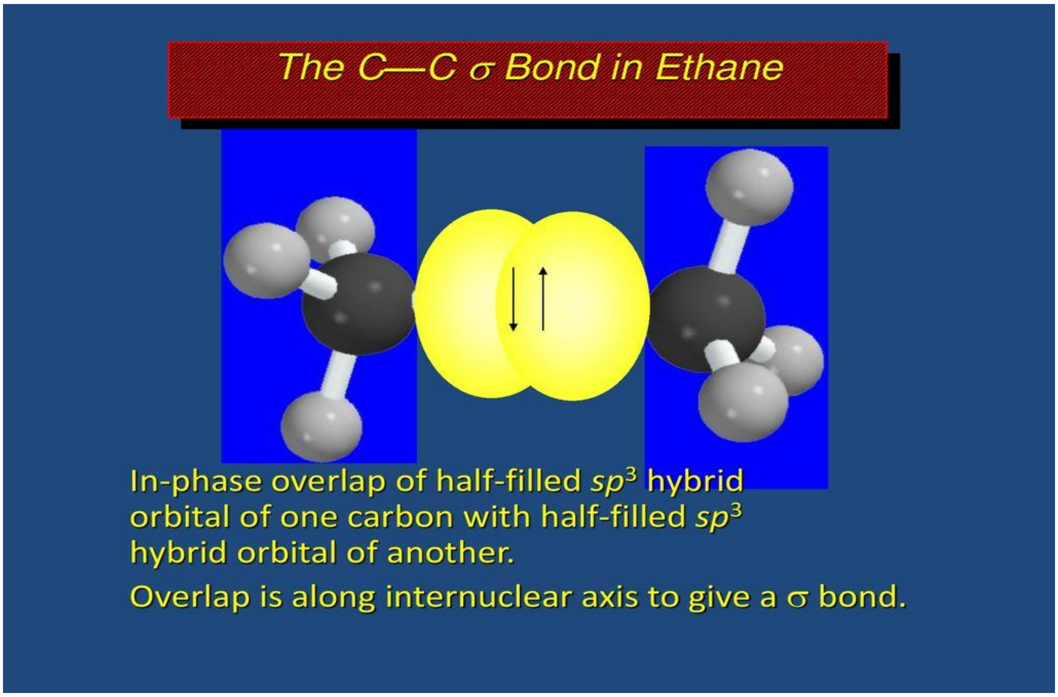




The C—C σ Bond in Ethane

In-phase overlap of half-filled sp^3 hybrid orbital of one carbon with half-filled sp^3 hybrid orbital of another.

Overlap is along internuclear axis to give a σ bond.



The C—C σ Bond in Ethane

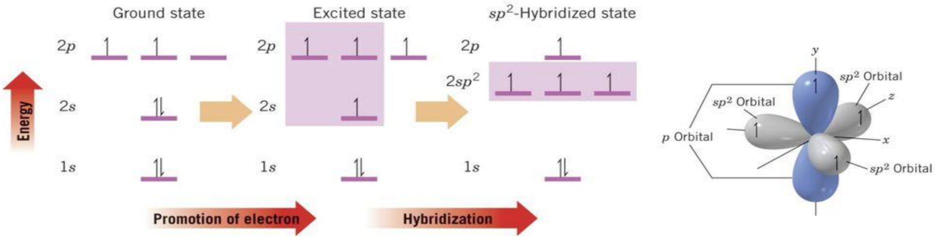
In-phase overlap of half-filled sp^3 hybrid orbital of one carbon with half-filled sp^3 hybrid orbital of another.

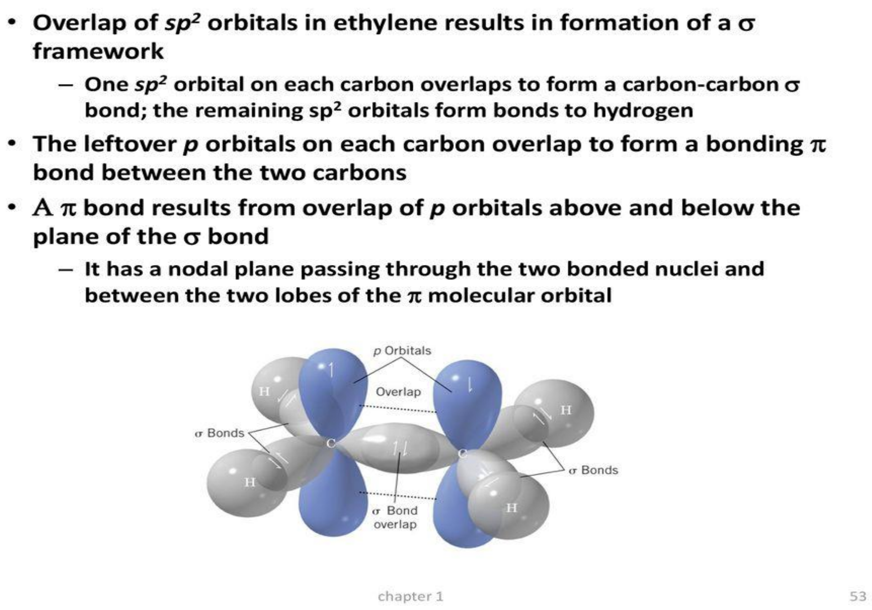
Overlap is along internuclear axis to give a σ bond.

hybrid orbitals — sp, sp^2, or sp^3

formation of σ bond

- **There are three σ bonds around each carbon of ethene and these are formed by using *sp²* hybridized orbitals**
- **The three *sp²* hybridized orbitals come from mixing one *s* and two *p* orbitals**
  - **One *p* orbital is left unhybridized**
- **The *sp²* orbitals are arranged in a trigonal planar arrangement**
  - **The *p* orbital is perpendicular (orthoganol) to the plane**





- **Overlap of *sp*^{2} orbitals in ethylene results in formation of a σ framework**
  - **One *sp*^{2} orbital on each carbon overlaps to form a carbon-carbon σ bond; the remaining sp^2 orbitals form bonds to hydrogen**
- **The leftover *p* orbitals on each carbon overlap to form a bonding π bond between the two carbons**
- **A π bond results from overlap of *p* orbitals above and below the plane of the σ bond**
  - **It has a nodal plane passing through the two bonded nuclei and between the two lobes of the π molecular orbital**

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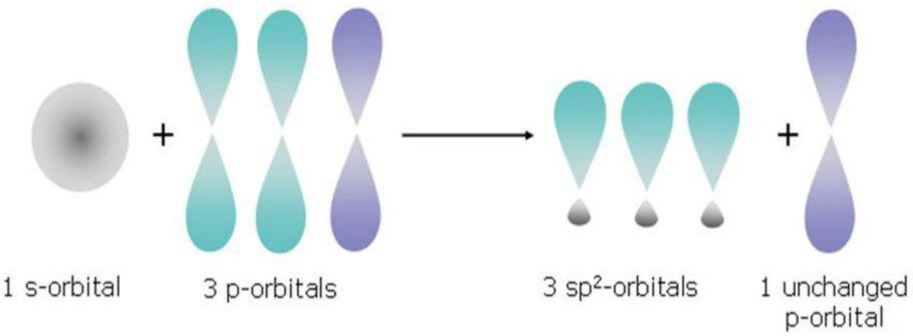
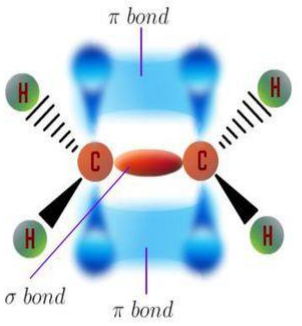
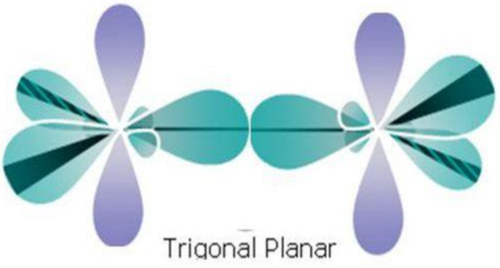
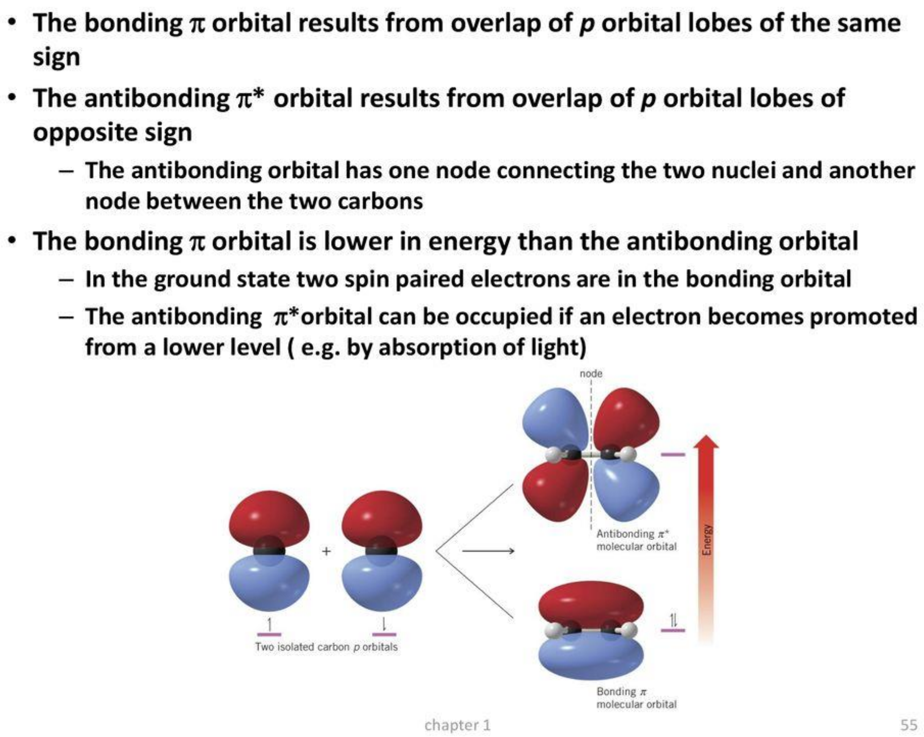
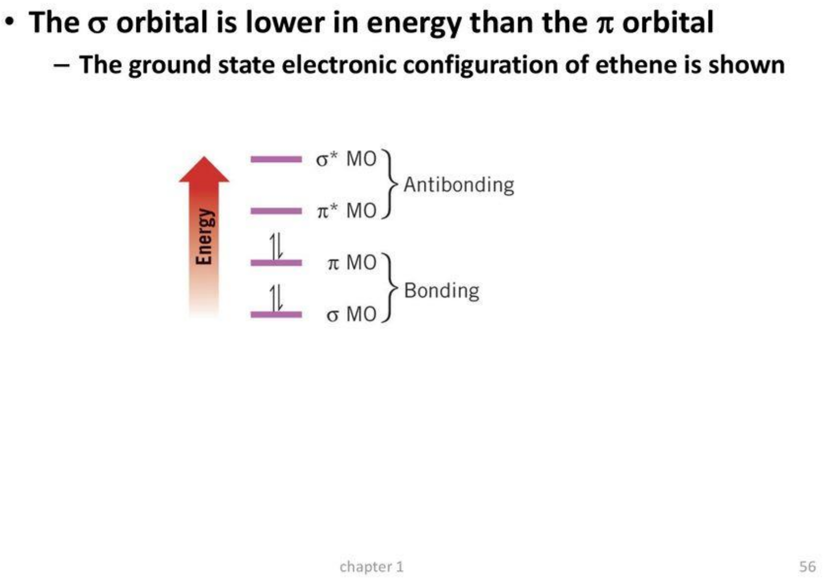




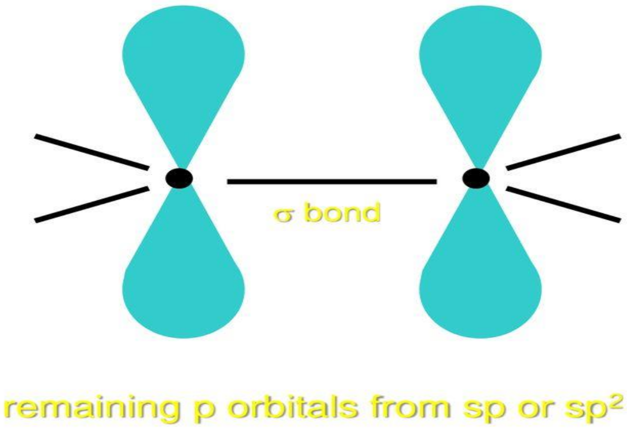


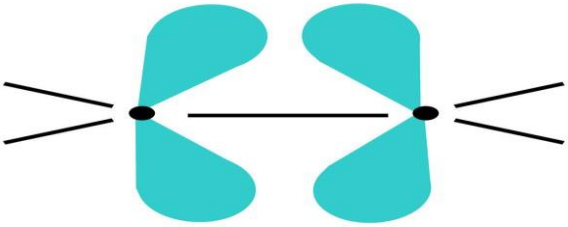


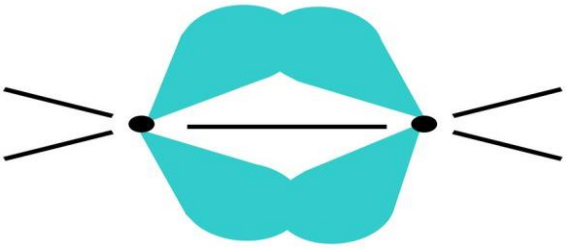
- **The bonding π orbital results from overlap of *p* orbital lobes of the same sign**
- **The antibonding π* orbital results from overlap of *p* orbital lobes of opposite sign**
  - **The antibonding orbital has one node connecting the two nuclei and another node between the two carbons**
- **The bonding π orbital is lower in energy than the antibonding orbital**
  - **In the ground state two spin paired electrons are in the bonding orbital**
  - **The antibonding π*orbital can be occupied if an electron becomes promoted from a lower level (e.g. by absorption of light)**

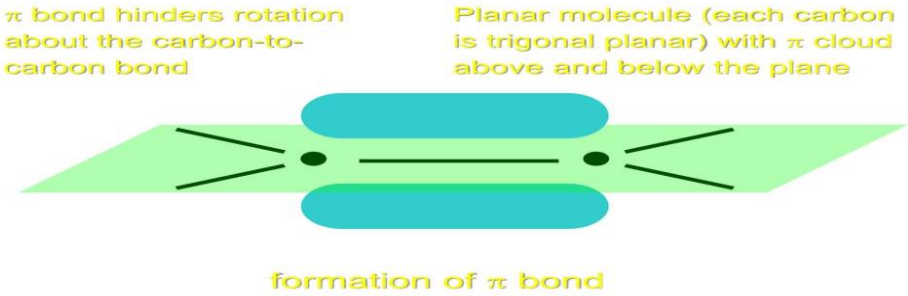


- **The σ orbital is lower in energy than the π orbital**
  - **The ground state electronic configuration of ethene is shown**


σ bond
remaining p orbitals from sp or sp²



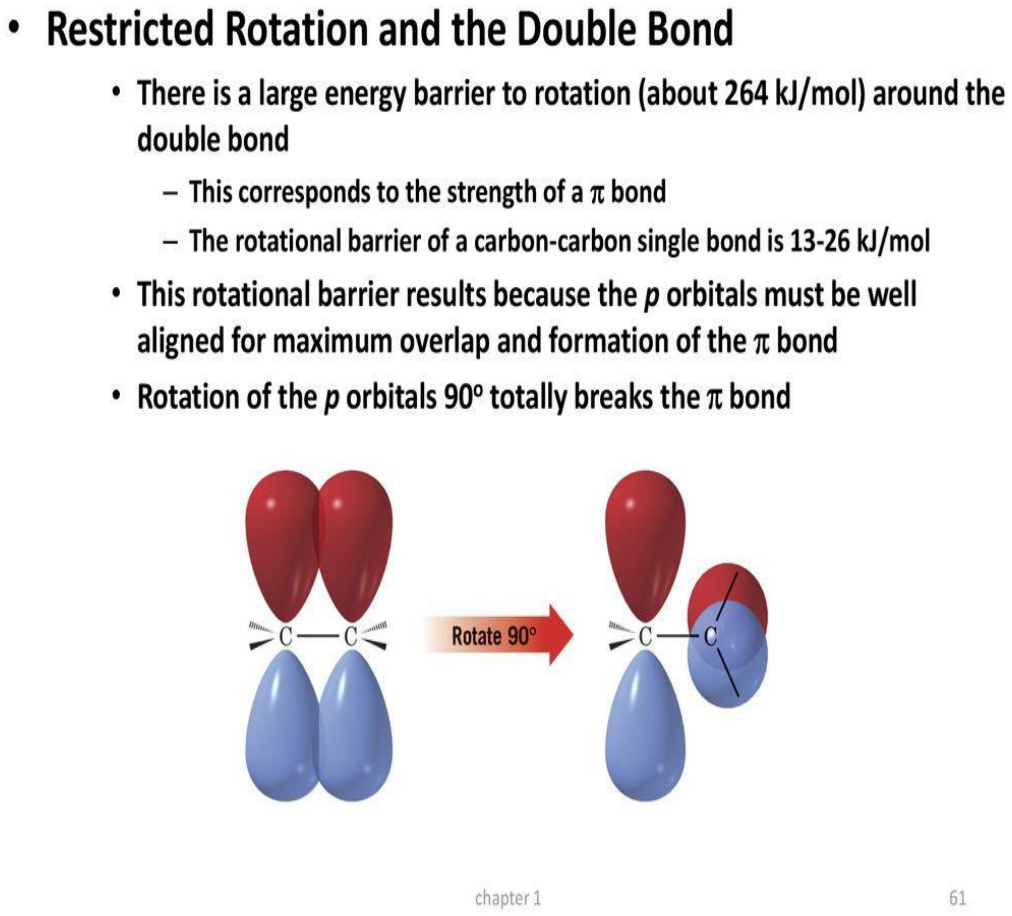




π bond hinders rotation about the carbon-to-carbon bond

Planar molecule (each carbon is trigonal planar) with π cloud above and below the plane

formation of π bond



- **Restricted Rotation and the Double Bond**
  - There is a large energy barrier to rotation (about 264 kJ/mol) around the double bond
    - This corresponds to the strength of a π bond
    - The rotational barrier of a carbon-carbon single bond is 13-26 kJ/mol
  - This rotational barrier results because the *p* orbitals must be well aligned for maximum overlap and formation of the π bond
  - Rotation of the *p* orbitals 90° totally breaks the π bond

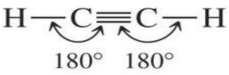
The Structure of Ethyne (Acetylene): *sp* Hybridization

- **Ethyne (acetylene) is a member of a group of compounds called alkynes which all have carbon-carbon triple bonds**
  - **Propyne is another typical alkyne**

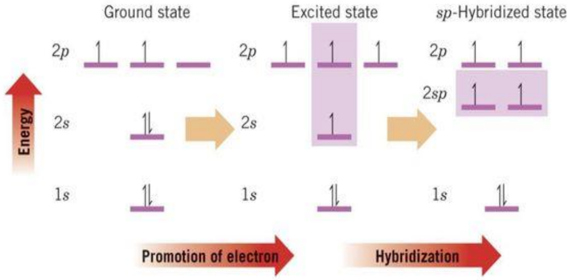
$H-C\equiv C-H$ **Ethyne (acetylene) (C_2H_2)**

$CH_3-C\equiv C-H$ **Propyne (C_3H_4)**

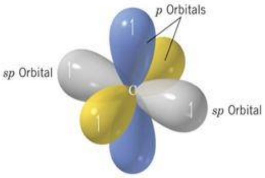
- **The arrangement of atoms around each carbon is linear with bond angles 180°**



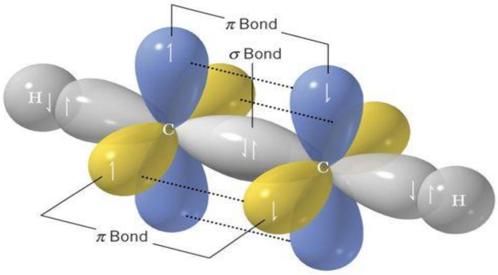
- **The carbon in ethyne is *sp* hybridized**
  - **One *s* and one *p* orbital are mixed to form two *sp* orbitals**
  - **Two *p* orbitals are left unhybridized**



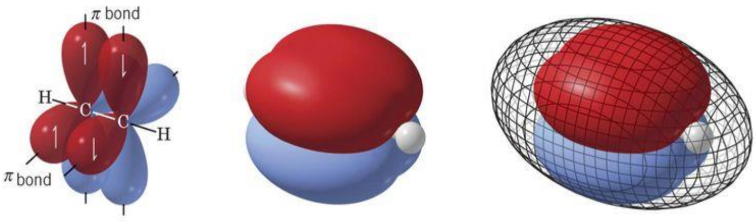
- **The two *sp* orbitals are oriented 180° relative to each other around the carbon nucleus**
  - **The two *p* orbitals are perpendicular to the axis that passes through the center of the *sp* orbitals**



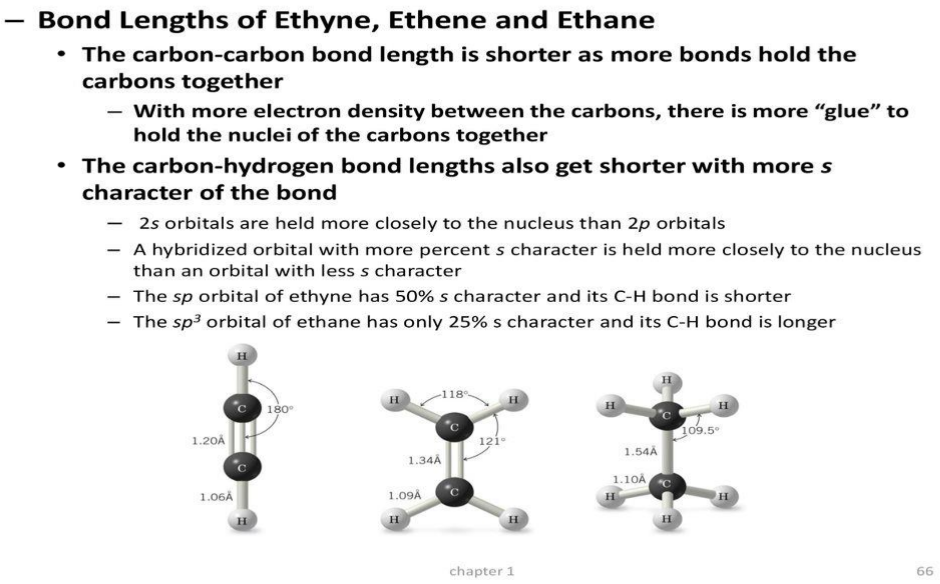
- **In ethyne the *sp* orbitals on the two carbons overlap to form a σ bond**
  - **The remaining *sp* orbitals overlap with hydrogen 1s orbitals**
- **The *p* orbitals on each carbon overlap to form two π bonds**
- **The triple bond consists of one σ and two π bonds**



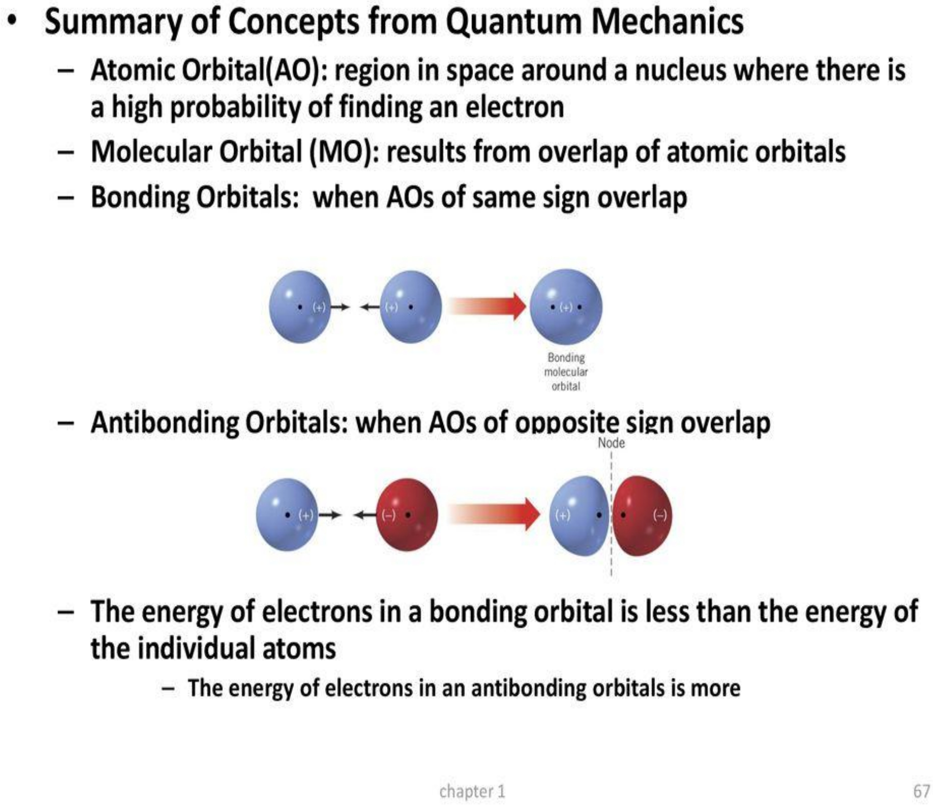
- **Depictions of ethyne show that the electron density around the carbon-carbon bond has circular symmetry**
  - **Even if rotation around the carbon-carbon bond occurred, a different compound would not result**



(*a*) (*b*) (*c*)



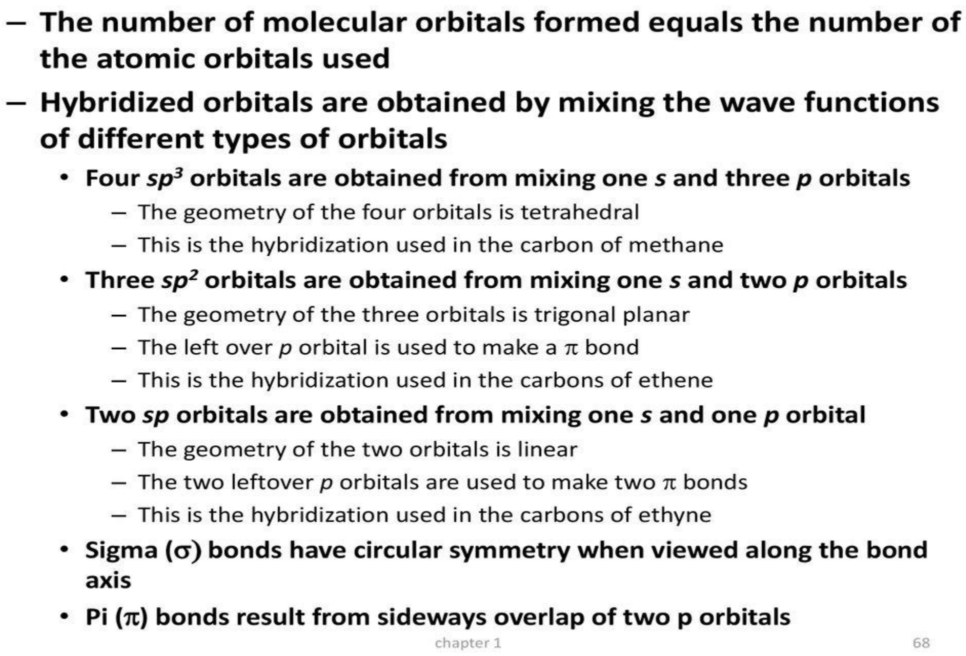
- **Bond Lengths of Ethyne, Ethene and Ethane**
  - **The carbon-carbon bond length is shorter as more bonds hold the carbons together**
    - **With more electron density between the carbons, there is more “glue” to hold the nuclei of the carbons together**
  - **The carbon-hydrogen bond lengths also get shorter with more *s* character of the bond**
    - 2*s* orbitals are held more closely to the nucleus than 2*p* orbitals
    - A hybridized orbital with more percent *s* character is held more closely to the nucleus than an orbital with less *s* character
    - The *sp* orbital of ethyne has 50% *s* character and its C-H bond is shorter
    - The sp^3 orbital of ethane has only 25% s character and its C-H bond is longer



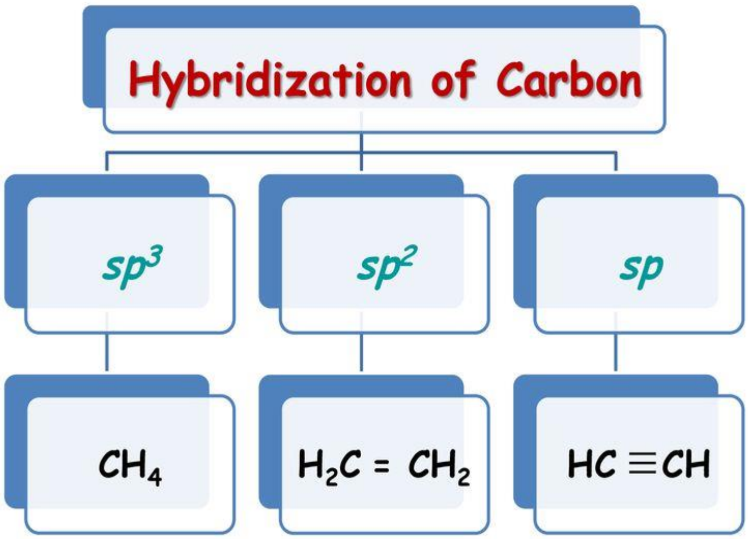
- **Summary of Concepts from Quantum Mechanics**
  - **Atomic Orbital(AO): region in space around a nucleus where there is a high probability of finding an electron**
  - **Molecular Orbital (MO): results from overlap of atomic orbitals**
  - **Bonding Orbitals: when AOs of same sign overlap**

  - **Antibonding Orbitals: when AOs of opposite sign overlap**

  - **The energy of electrons in a bonding orbital is less than the energy of the individual atoms**
    - **The energy of electrons in an antibonding orbitals is more**



- The number of molecular orbitals formed equals the number of the atomic orbitals used
- Hybridized orbitals are obtained by mixing the wave functions of different types of orbitals
  - **Four sp^3 orbitals are obtained from mixing one *s* and three *p* orbitals**
    - The geometry of the four orbitals is tetrahedral
    - This is the hybridization used in the carbon of methane
  - **Three sp^2 orbitals are obtained from mixing one *s* and two *p* orbitals**
    - The geometry of the three orbitals is trigonal planar
    - The left over *p* orbital is used to make a π bond
    - This is the hybridization used in the carbons of ethene
  - **Two *sp* orbitals are obtained from mixing one *s* and one *p* orbital**
    - The geometry of the two orbitals is linear
    - The two leftover *p* orbitals are used to make two π bonds
    - This is the hybridization used in the carbons of ethyne
  - **Sigma (σ) bonds have circular symmetry when viewed along the bond axis**
  - **Pi (π) bonds result from sideways overlap of two p orbitals**



Hybridization of Carbon

sp^3 sp^2 sp

CH_4 $H_2C = CH_2$ $HC \equiv CH$

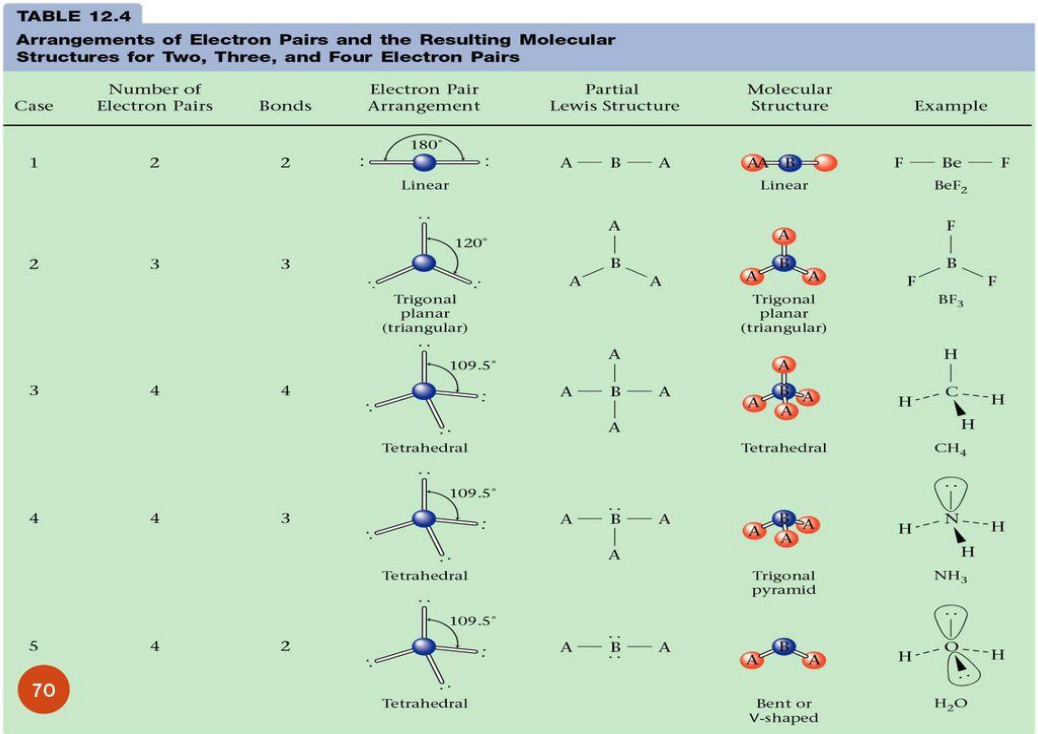


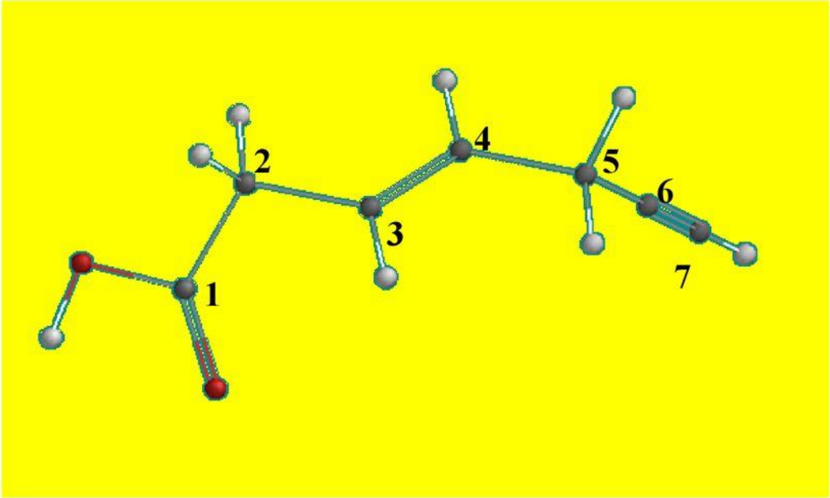
TABLE 12.4

Arrangements of Electron Pairs and the Resulting Molecular Structures for Two, Three, and Four Electron Pairs

Case	Number of Electron Pairs	Bonds	Electron Pair Arrangement	Partial Lewis Structure	Molecular Structure	Example
1	2	2	180° Linear	A — B — A	Linear	F — Be — F BeF_2
2	3	3	120° Trigonal planar (triangular)	A B A A	Trigonal planar (triangular)	F B F F BF_3
3	4	4	109.5° Tetrahedral	A A — B — A A	Tetrahedral	H H C H H CH_4
4	4	3	109.5° Tetrahedral	A — $\ddot{B}$ — A A	Trigonal pyramid	H N H H NH_3
5	4	2	109.5° Tetrahedral	A — B — A	Bent or V-shaped	H O H H_2O

70

What is the hybridization in each carbon atom?

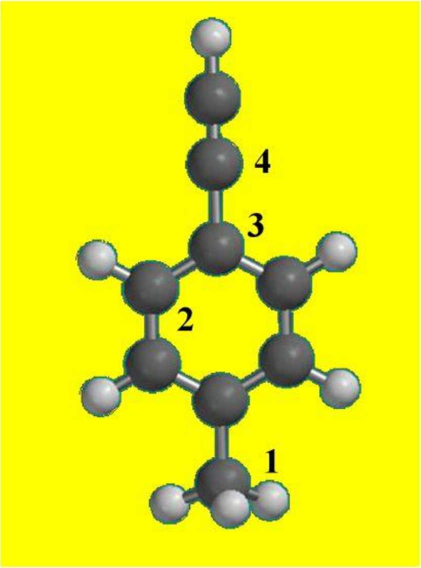


sp^3 – 2, 5 **tetrahedral**

sp^2 – 1, 3, 4 **trigonal planar**

sp – 6, 7 **linear**

What is the hybridization in each carbon atom?



What is pencil lead made of if it isn't lead?

Pencil lead is a mixture of graphite and clay.
Graphite is one form of the element carbon.
Other forms of carbon are diamond - the hardest naturally occurring substance on the earth, soot, charcoal and coke.

Pencils used to be made with lead, many years ago. Lead is poisonous and so sucking the end of your pencil could be quite dangerous.
We now use graphite and clay because it is safer and because we can make pencils of different hardness.

Chemistry of Living Things:

Living things are a lot like laboratories…

There's some serious chemistry going on inside.

Your body is an incredibly complex chemical machine taking in chemicals & food, and causing countless reactions to occur every second.

Biochemistry is the study of substances & processes occurring in all living organisms.

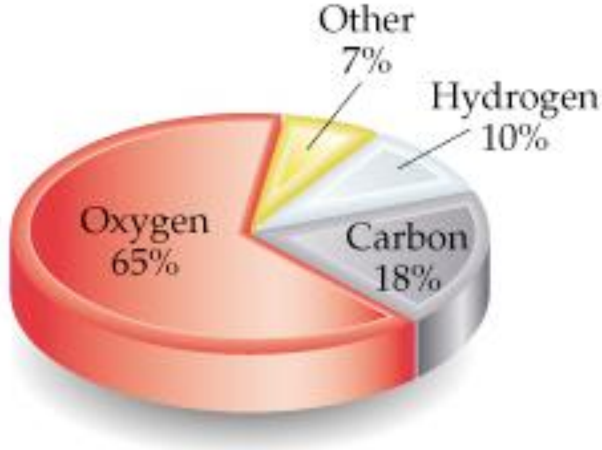
I'm made of what???

Guess how many elements your body is made up of?

25 elements make up all living things

About 97% of your body's mass is made of just 4 elements: oxygen, carbon, hydrogen, & nitrogen.

Two other major elements are phosphorous & sulfur.



Human body

Minor Elements:

Of course, other elements are also important, but they're often found in small amounts.

They may seem insignificant, but they're not.

For example, iron makes up only 0.004% of your body mass, but you can't live without it!

Major Compounds:

The human body also relies on many compounds, especially water & salt.

The human body typically consists of 60-65% water.

In other words, 2/3 of your body weight is water.

Water is important because many of our body's chemical reactions can only occur in solutions containing water.

Blood, sweat, urine… all mostly water!

Salt is also important because of how it can separate into its two ions: Na^+ and Cl^-.

Sodium ions regular the amount of water in our cells, while chlorine ions help our body digest food.

The most important element is…

Carbon

If you take away the water, the rest of the human body is 53% carbon.

It may not be the most abundant element in living things, but it certainly is the most important. At one time, scientists thought that the chemical reactions that took place inside of living things could not occur outside of them.

The carbon molecules were so complex, scientists thought they must have been made in some unknown way. They called these carbon compounds organic compounds.

The word “organic” has lots of meanings. Eventually, scientists realized that the reactions occurring inside the body could occur outside it as well.

They also learned how important carbon is in all living things, because of its ability to bond with other atoms.

Forms of Carbon

Diamond

Graphite

Charcoal

Not all substances made of carbon are living. Diamonds & graphite are pure forms of carbon.

Non-organic carbon compounds, and compounds without carbon, are called <u>inorganic</u> compounds.

What is organic chemistry?

We used to describe organic chemistry as the chemistry of living things.

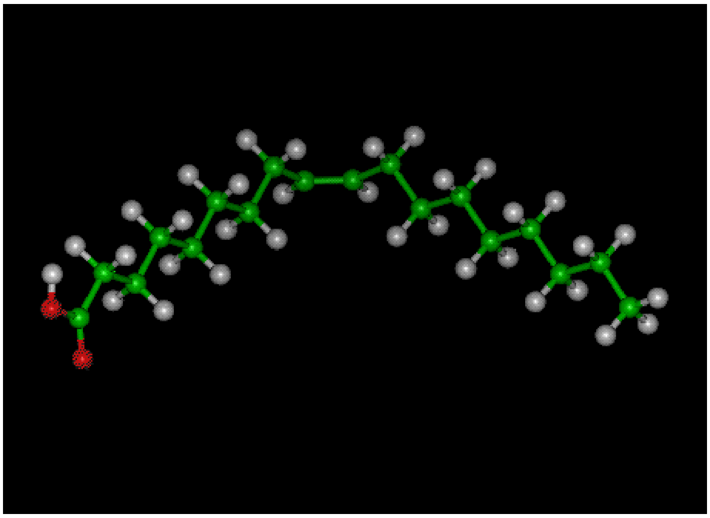
Since the chemistry of living things is based on carbon, the chemistry of carbon compounds has come to be known as organic chemistry.

It now includes the study of carbon compounds which are not found in living things and so is an incredibly large branch of modern chemistry.

Why is life based on the element carbon?

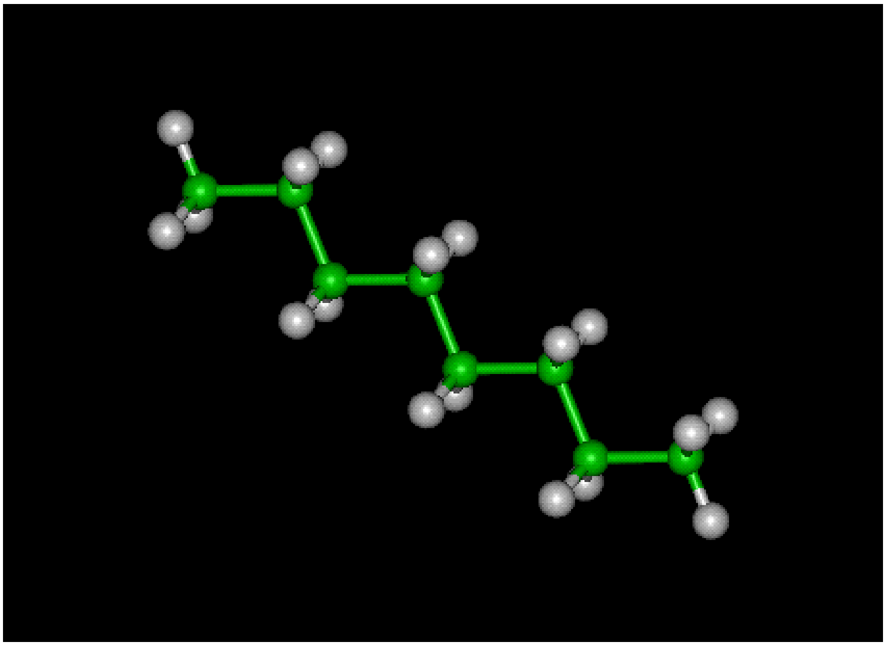
There are two important properties of carbon that make it a suitable element to form the compounds in living things:

Firstly, carbon atoms can link together to form stable chains of great length.



Carbon atoms bind strongly to each other and form very large molecules which are built around this carbon 'backbone'.

The covalent bond between two carbon atoms is strong so that the backbones are stable. In all of these compounds simple sub-units called monomers are linked together by condensation reactions.



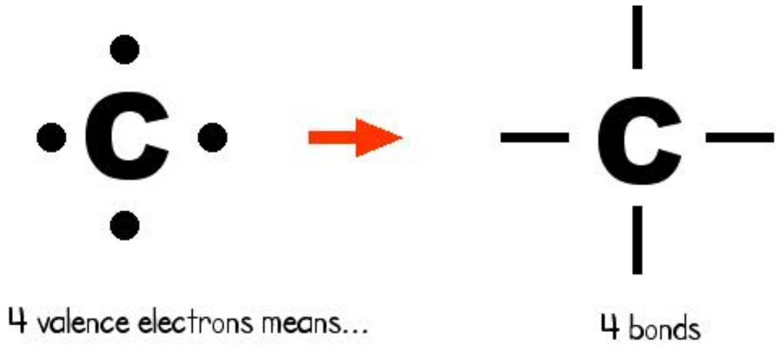
What makes carbon so special?

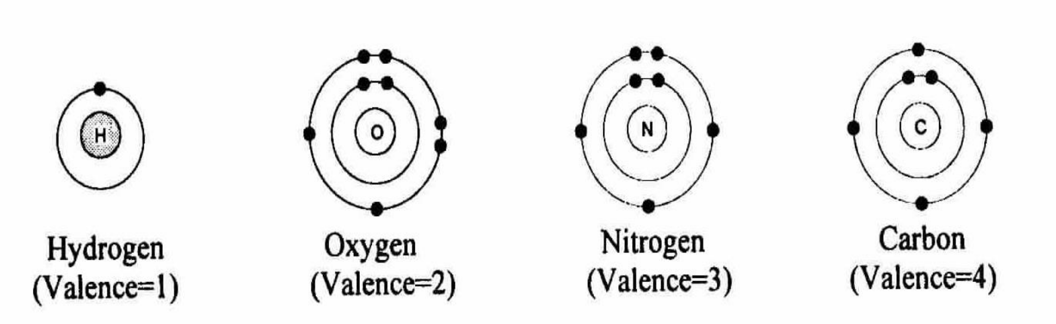
It has a "central" role in all living organisms.

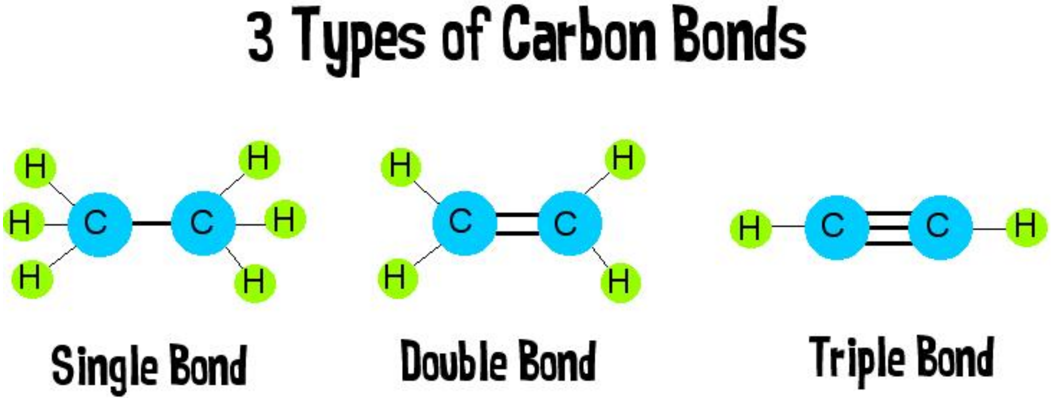
It has 4 valence electrons.

It makes 4 covalent bonds.

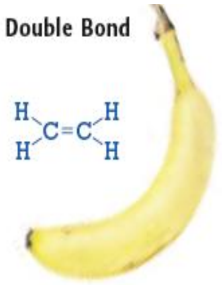
It can bond with any element, but really loves to bond with other carbon atoms and make long chains.





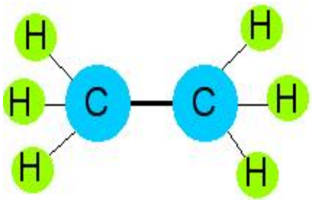


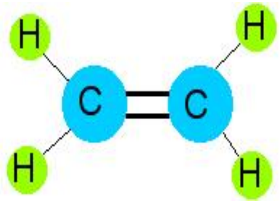
The **propane** in this camping stove contains only single bonds.

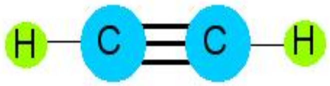


Fruits make **ethene,** which is a compound that helps ripen the fruit.

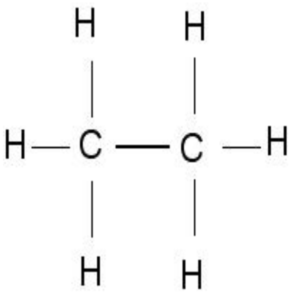
Ethyne is better known as *acetylene*. It is burned in this miner's lamp and in welding torches.

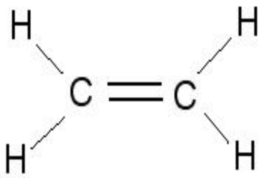






Full Structural Formulas





$H-C\equiv C-H$

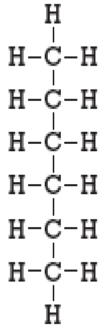
Simplified Structural Formulas

CH_3-CH_3

$CH_2=CH_2$

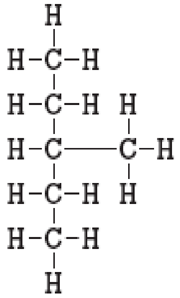
$CH\equiv CH$

3 Types of Carbon Backbones:



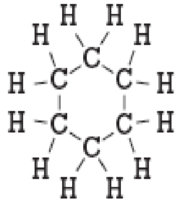
Straight chain

Carbon atoms are connected one after another.



Branched chain

The chain of carbon atoms branches when a carbon atom bonds to more than two other carbon atoms.



Ring

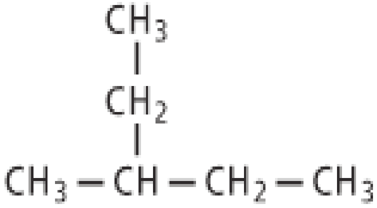
The chain of carbon atoms forms a ring.

Carbon forms long chains:

Straight Chain

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

Branched Chain



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

One carbon chain may contain hundreds of carbon atoms.

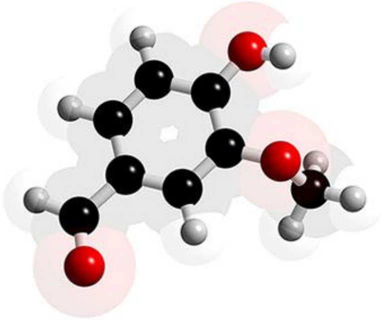
Unlike other elements, carbon atoms can bond to each other to form very long chains.

One carbon chain may contain hundreds of carbon atoms. Notice how the CH_2 units repeat.

A very large carbon-based molecule made of repeating units is called a polymer. Each unit of a polymer is called a monomer.

Polymers can be *thousands* of atoms long.

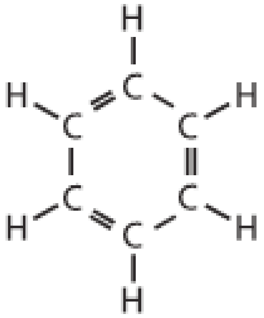
Carbon forms Rings:



Carbon-based molecules also can be shaped like rings. Most carbon rings contain 5 or 6 carbon atoms.

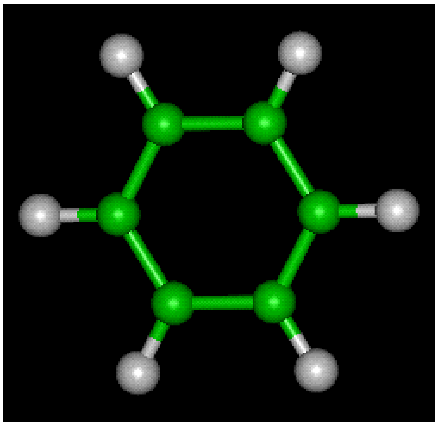
One of the most important carbon rings is benzene.

It has 6 carbons & 6 hydrogens, with alternating double bonds.



Benzene Ring

Simplified Benzene Ring



Many compounds are based on Benzene.

They often have very strong smells or aromas, so they are called aromatic compounds.

An example of one aromatic compound is a molecule called vanillin.

Guess what that smells like!

Silicon is similar to carbon. Why is there no life forms based on silicon?

Silicon is unsuitable because, although it is a valence IV element like carbon (4 electrons to share), BUT the silicon-silicon covalent bond is not strong enough for it to form long stable chains.

So, it cannot form molecules of the complexity needed to make up cells like carbon can!

Long Chain Hydrocarbons & their Names:

The alkanes make up a series of saturated hydrocarbons, called a homologous series because they have similar properties and have the same general formula:

The first four members of the series are gases at room temperature and are called:

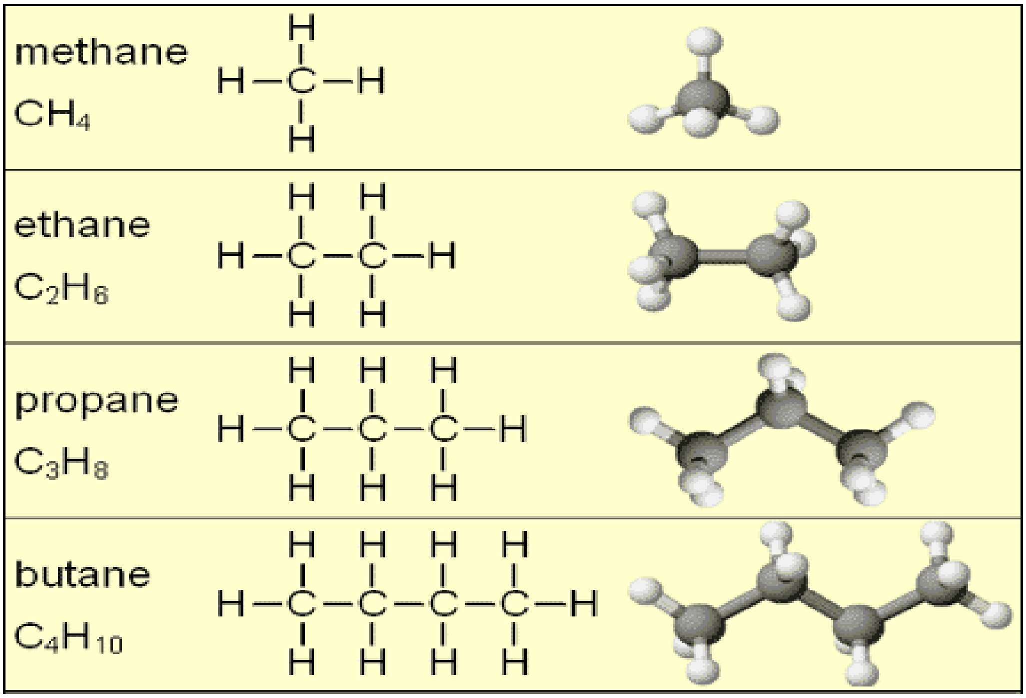
methane, CH_4

ethane, C_2H_6

propane, C_3H_8

butane, C_4H_{10}

Alkanes



methane	CH_4
ethane	C_2H_6
propane	C_3H_8
butane	C_4H_{10}

Alkanes with increasing numbers of carbon atoms have names are based on the Greek word for the number of carbon atoms in the chain of each molecule.

So you can get, for example,

pentane (5),

hexane (6),

heptane (7)

and octane (8).

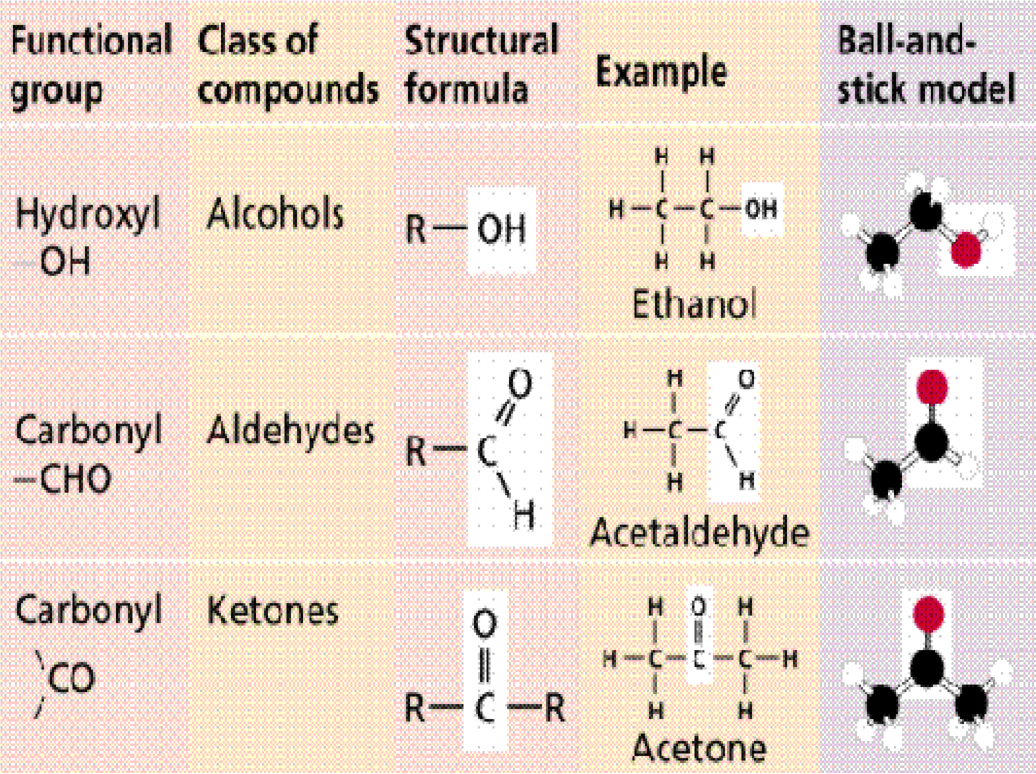
From pentane onwards, approximately the next thirty alkanes in the series are liquids.

Alkanes with even longer chains are waxy solids.

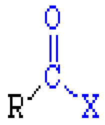
They are typical covalent compounds, insoluble in water but able to mix with each other. Alkanes burn in oxygen to produce carbon dioxide and steam.

Classification of organic compounds

Related compounds that have the same functional group (groups of atoms found within molecules that are involved in the chemical reactions characteristic of those molecules).



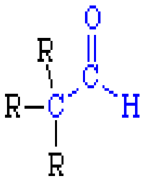
Functional group	Class of compounds	Structural formula	Example	Ball-and-stick model
Hydroxyl –OH	Alcohols	$R-OH$	$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$ Ethanol	
Carbonyl –CHO	Aldehydes	$R-C(=O)-H$	$H-\underset{H}{\overset{H}{C}}-C(=O)-H$ Acetaldehyde	
Carbonyl >CO	Ketones	$R-\overset{O}{\overset{\|}{C}}-R$	$H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-H$ Acetone	



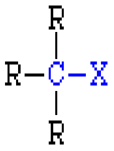
acyl halides
(X = F, Cl, Br, I)

$R-O-H$

alcohols



aldehydes

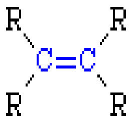


$R-\overset{R}{\underset{R}{C}}-X$

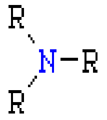
alkyl halides
(X = F, Cl, Br, I)

$R-C\equiv C-R$

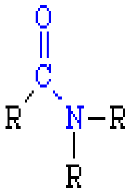
alkynes



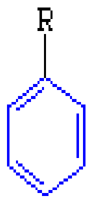
alkenes



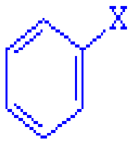
amines



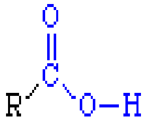
amides



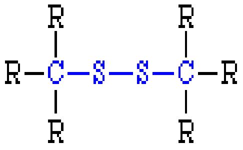
aromatic rings



aryl halides
(X = F, Cl, Br, I)

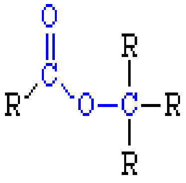


carboxylic acids

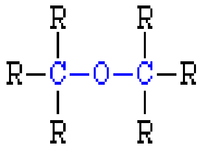


$R-\overset{R}{\underset{R}{C}}-S-S-\overset{R}{\underset{R}{C}}-R$

disulfides

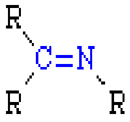


esters

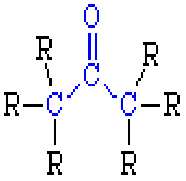


$R-\overset{R}{\underset{R}{C}}-O-\overset{R}{\underset{R}{C}}-R$

ethers



imines



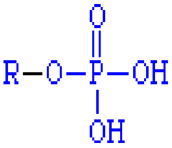
ketones

$R-C\equiv N$

nitriles

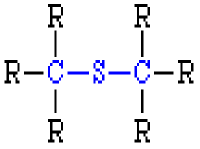
$R-NO_2$

nitro groups



$R-O-\overset{O}{\underset{OH}{P}}-OH$

phosphate esters



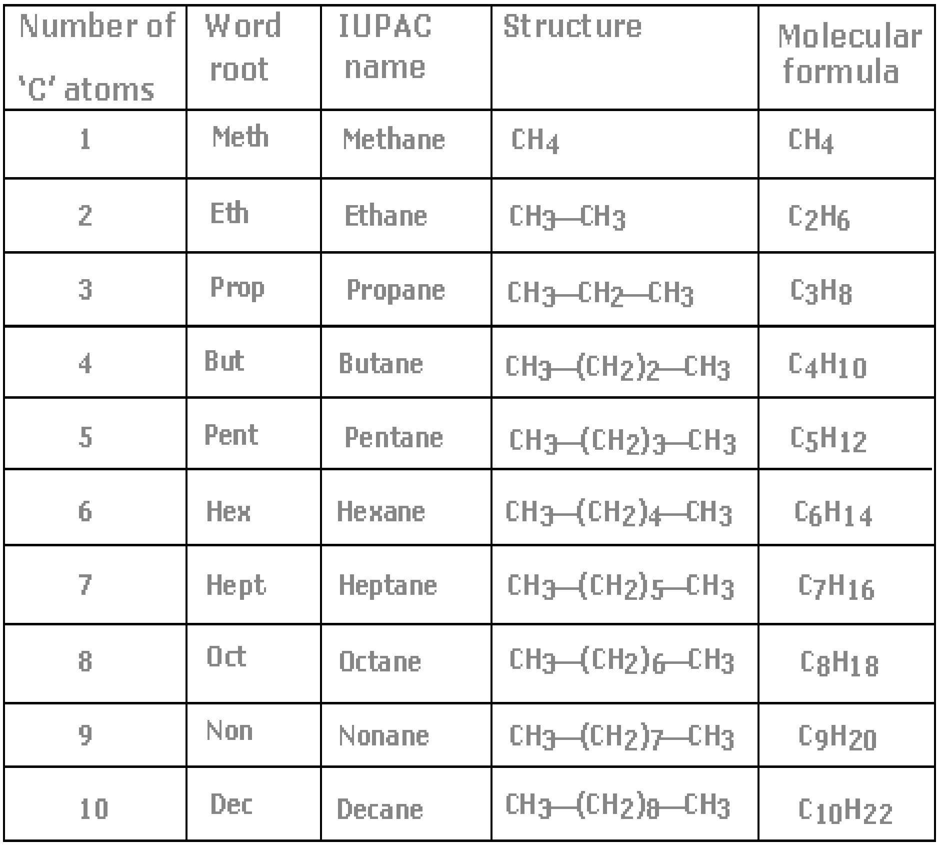
$R-\overset{R}{\underset{R}{C}}-S-\overset{R}{\underset{R}{C}}-R$

thioethers

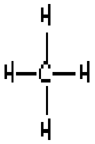
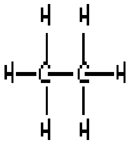
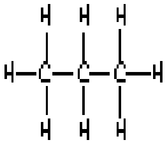
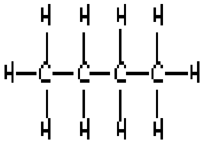
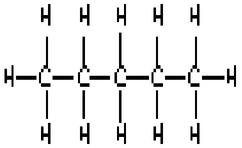
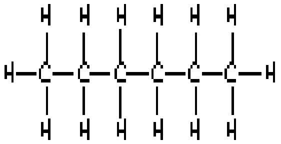
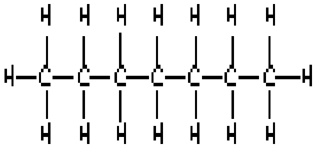
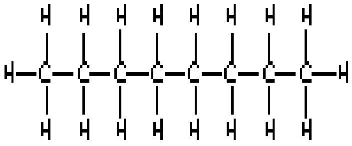
$R-S-H$

thiols

- **differ from each other by a CH_2 unit can be represented by a general formula**
  - **examples: C_nH_{2n+2} (alkanes) or C_nH_{2n} (alkenes) or…**



Number of 'C' atoms	Word root	IUPAC name	Structure	Molecular formula
1	Meth	Methane	CH_4	CH_4
2	Eth	Ethane	CH_3-CH_3	C_2H_6
3	Prop	Propane	$CH_3-CH_2-CH_3$	C_3H_8
4	But	Butane	$CH_3-(CH_2)_2-CH_3$	C_4H_{10}
5	Pent	Pentane	$CH_3-(CH_2)_3-CH_3$	C_5H_{12}
6	Hex	Hexane	$CH_3-(CH_2)_4-CH_3$	C_6H_{14}
7	Hept	Heptane	$CH_3-(CH_2)_5-CH_3$	C_7H_{16}
8	Oct	Octane	$CH_3-(CH_2)_6-CH_3$	C_8H_{18}
9	Non	Nonane	$CH_3-(CH_2)_7-CH_3$	C_9H_{20}
10	Dec	Decane	$CH_3-(CH_2)_8-CH_3$	$C_{10}H_{22}$

# Carbons	Name	Structure
1	methane	
2	ethane	
3	propane	
4	butane	
5	pentane	
6	hexane	
7	heptane	
8	octane	

Naming Organic Compounds

The name of any organic compound is comprised of three portions:

PREFIX + ROOT + SUFFIX

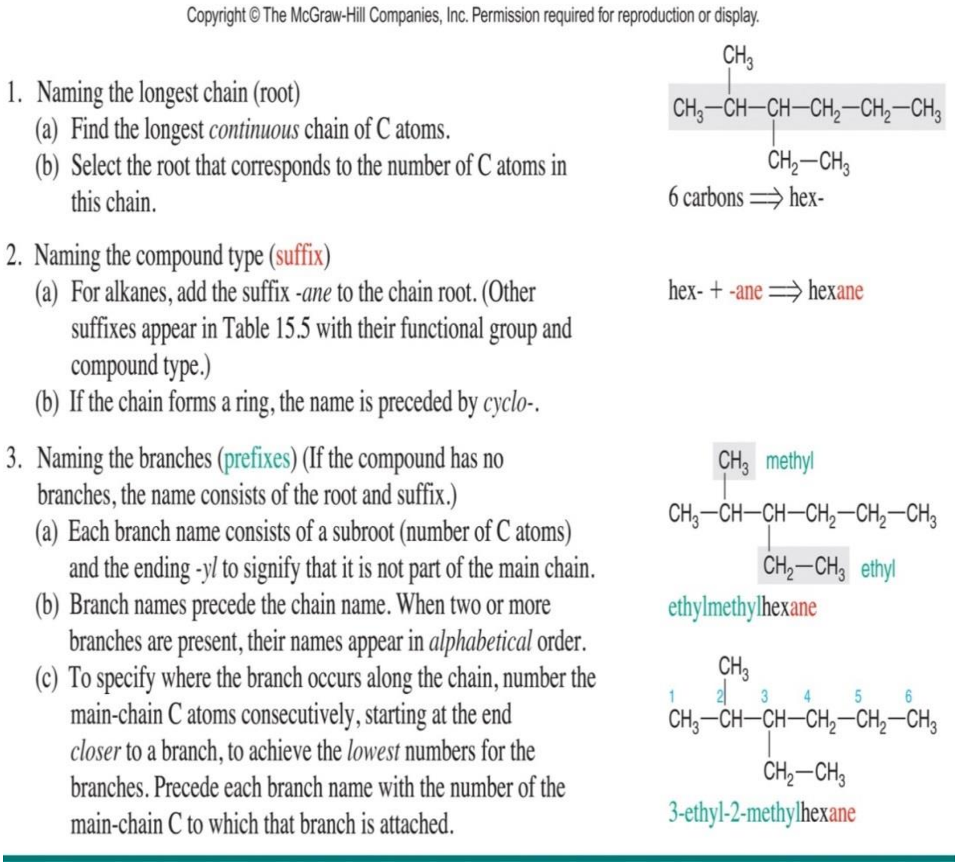
The *root* name of the compound is determined from the *number* of C atoms in the *longest continuous chain.* The *suffix* indicates the *type* of organic compound, and is placed after the root. The suffix for an alkane is –ane. The *prefix* identifies any groups attached to the main chain.

Numerical Roots for Carbon Chains and Branches

Roots	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7

oct-	**8**
non-	**9**
dec-	**10**

Rules for Naming an Organic Compound



1. Naming the longest chain (root)
   (a) Find the longest *continuous* chain of C atoms.
   (b) Select the root that corresponds to the number of C atoms in this chain.

6 carbons ⟹ hex-

2. Naming the compound type (suffix)
   (a) For alkanes, add the suffix *-ane* to the chain root. (Other suffixes appear in Table 15.5 with their functional group and compound type.)
   (b) If the chain forms a ring, the name is preceded by *cyclo-*.

hex- + -ane ⟹ hexane

3. Naming the branches (prefixes) (If the compound has no branches, the name consists of the root and suffix.)
   (a) Each branch name consists of a subroot (number of C atoms) and the ending *-yl* to signify that it is not part of the main chain.
   (b) Branch names precede the chain name. When two or more branches are present, their names appear in *alphabetical* order.
   (c) To specify where the branch occurs along the chain, number the main-chain C atoms consecutively, starting at the end *closer* to a branch, to achieve the *lowest* numbers for the branches. Precede each branch name with the number of the main-chain C to which that branch is attached.

ethylmethylhexane

3-ethyl-2-methylhexane

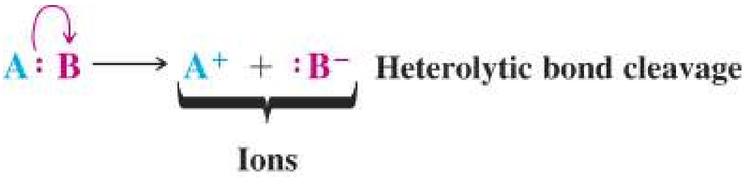
Chemical reaction (التفاعل الكيميائى)

بصفة عامة التفاعل الكيميائى فى مجمله عبارة عن كسر روابط كيميائية وتكوين روابط جديدة. ولذا يجب توضيح الكيفية التى يتم بها تكسير رابطة او تكوين رابطة أخرى.

Cleavage of Covalent Bonds (كيفية تكسير رابطة تساهمية)

a- Homolytic bond Cleavage: تكسير متماثل للرابطة

b- Heterolytic bond Cleavage: تكسير غير متماثل للرابطة



Bond making (كيفية تكوين رابطة)

a- Homogenic bond making (تكوين متماثل للرابطة)

أمثلة: تفاعلات جذور حرة

b- Heterogenic bond making (تكوين غير متماثل للرابطة)

أمثلة: تفاعلات قطبية أو قطبية نسبية

Types of Reactions and Their Mechanisms

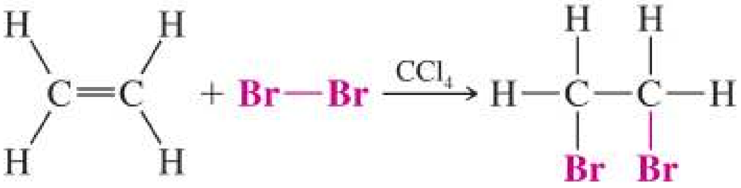
بصفة عامة يمكن تقسيم التفاعلات العضوية الى أربع أنواع من التفاعلات.

1- Substitution reactions تفاعلات استبدال

$$H_3C{-}Cl + Na^+OH^- \xrightarrow{H_2O} H_3C{-}OH + Na^+Cl^-$$

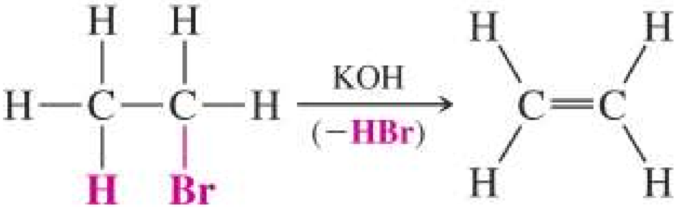
A substitution reaction

2- Addition reactions تفاعلات اضافة



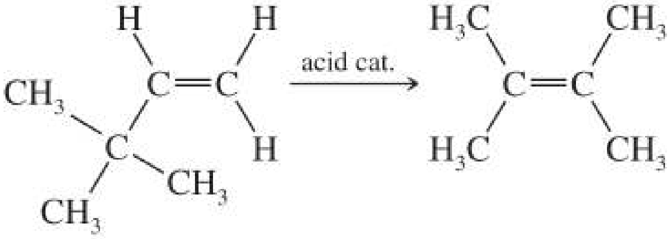
An addition reaction

3- Elimination reactions تفاعلات نزع



An elimination reaction

4- Rearrangement reactions تفاعلات اعادة ترتيب



A rearrangement

26

HYDROCARBONS

You have studied in the previous lesson that hydrocarbons are the compounds containing carbon and hydrogen. You also know that they are classified as aliphatic, alicyclic and aromatic hydrocarbons. They constitute a very important class of organic compounds and are widely used as fuels, lubricants and dry cleaning agents. They are also used as important ingredients in medicines and in dyes. Petroleum and coal are the major sources of various types of hydrocarbons. The products obtained from fractional distillation of petroleum and destructive distillation of coal are used almost in every sphere of life. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with different functional groups. In this lesson, you will study about the preparation, important physical and chemical properties of hydrocarbons.

Objectives

After reading this lesson, you will be able to :

- list different methods of preparation of alkanes;
- explain the reasons for variation in physical properties of alkanes;
- describe different chemical properties of alkanes;
- list different methods of preparation of alkenes;
- explain the physical properties of alkenes;
- describe the chemical properties of alkenes;
- list different methods of preparation of alkynes;
- explain physical and chemical properties of alkynes;
- discuss the cause of greater reactivity of alkenes and alkynes over alkanes;
- distinguish alkanes, alkenes and alkynes;
- list various fractions obtained by destructive distillation of coal;
- explain the stability of various organic compounds using resonance;

- describe methods of preparation, physical properties and chemical properties of benzene, and
- list various uses of hydrocarbons.

26.1 Alkanes (Paraffins)

Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as *paraffins* (*parum* means little, *affins* means affinity).

26.1.1 Methods of Preparation

Some important methods of preparation of alkanes are as follows:

1. **From Haloalkanes (Alkyl Halides):** Monohaloalkanes can be converted to alkanes by following three methods :

   a) **By reduction of haloalkanes:** The replacement of halogen atom of haloalkanes with hydrogen is called the reduction and can be carried out by the following reagents :

   (i) Zinc and dilute HCl

$$\underset{\textbf{Bromomethane}}{CH_3Br} + Zn + 2\,HCl \longrightarrow \underset{\textbf{Methane}}{CH_4} + ZnCl_2 + HBr$$

   (ii) HI in the presence of red phosphorus

$$\underset{\textbf{Iodoethane}}{C_2H_5I} + HI \xrightarrow[\text{423 K}]{\text{red phosphorus}} \underset{\textbf{Methane}}{C_2H_6} \quad ZnCl_2 \quad HBr$$

   (iii) Catalytic reduction

$$\underset{\textbf{Chloromethane}}{CH_3Cl} + H_2 \xrightarrow{\text{Pt (catalyst)}} \underset{\textbf{Methane}}{CH_4} \quad HCl$$

   b) **By using Grignard's Reagent :** A Grignard reagent is a compund of the type RMgX which is prepared by reacting a haloalkane with magnesium metal in the presence of dry ether.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br} + Mg \xrightarrow{\text{dry ether}} \underset{\textbf{Ethyl Magnesium Bromide}}{C_2H_5MgBr}$$

   The Grignard's reagents are used to prepare various compounds like hydrocarbons, ethers, alcohols and carboxylic acids. It reacts with the compounds containing active hydrogen and forms alkanes. An easily replaceable hydrogen atom present in the compounds is called *active hydrogen*. An active hydrogen is present in (i) alcohols and (ii) water and (iii) acids.

$$CH_3MgBr + C_2H_5OH \rightarrow CH_4 + Mg(OC_2H_5)Br$$

$$C_2H_5MgBr + H_2O \rightarrow C_2H_6 + Mg(OH)Br$$

   c) **By Wurtz Reaction :** In this reaction, an alkyl halide reacts with sodium metal in the presence of dry ether and forms the higher alkanes.

$$\underset{\textbf{Bromoethane}}{CH_3-Br+2\,Na+Br-CH_3} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethane}}{CH_3-CH_3}+2\,NaBr$$

2. **From Unsaturated Hydrocarbons :** The unsaturated hydrocarbons (i.e. alkenes and alkynes) can be converted to alkanes by the addition of hydrogen in the presence of a catalyst like nickel, platinum or palladium.

$$CH_2=CH_2+H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3-CH_3$$

$$CH\equiv CH+2H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3-CH_3$$

This reaction is also called **hydrogenation** and is used to prepare vegetable ghee from edible oils (by converting unsaturated fats to saturated ones.)

3. **From Alcohols, Aldehydes and Ketones :** Alcohols, aldehydes and ketones on reduction with HI, in presence of red phosphorus, give alkanes.The general reactions are as shown below.

$$\underset{\textbf{Alcohol}}{ROH}+2HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RH}+I_2+H_2O$$

$$\underset{\textbf{Aldehyde}}{RCHO}+4HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RCH_3}+2\,I_2+H_2O$$

$$\underset{\textbf{Ketone}}{RCOR'}+4HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RCH_2R'}+2\,I_2+H_2O$$

4. **From Carboxylic Acids :** Carboxylic acids can produce alkanes in a number of ways as shown below :

i) Heating with soda lime : $RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$

In this reaction, an alkane with one carbon less than those present in the parent carboxylic acid is obtained.

ii) By Reduction of carboxylic acid:

$$RCOOH\ +\ 6\,HI \xrightarrow{\text{red P / 423 K}} RCH_3+3\,I_2+2H_2O$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe's Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The reaction takes place as follows.

$$\underset{\textbf{Sodium salt of carboxylic acid}}{RCOONa} \xrightarrow{\text{electrolysis}} \underset{\textbf{Anion}}{RCOO^-}+\underset{\textbf{Cation}}{Na^+}$$

At Anode :

$$RCOO^- \longrightarrow RCOO^\bullet + e^-$$

$$RCOO^\bullet \longrightarrow R^\bullet + CO_2$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$

Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\textbf{Sodium ethanote}}{2\,CH_3COONa} \longrightarrow \underset{\textbf{Ethane (at anode)}}{CH_3-CH_3}$$

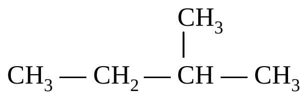
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

26.1.2 Physical Properties of Alkanes

Physical State: The physical state of alkanes depends upon the intermolecular forces of attraction present between molecules which in turn, depend upon the surface area of the molecules. *As the molecular mass of the alkanes increases, their surface area also increases, which in turn, increases the intermolecular forces of attraction, and accordingly, the physical state of alkanes changes from gaseous to liquid, and then to solid.* The alkanes containing 1 to 4 carbon atoms are gases, whereas those containing 5 to 17 carbon atoms are liquids, and the still higher ones are solids. In the case of isomeric alkanes, the straight chain alkanes will have maximum surface area, and hence, stronger intermolecular force of attraction. As the branching increases, surface area decreases. Hence the intermolecular forces of attraction decrease. Let us consider the isomers of pentane (C_5H_{12}).

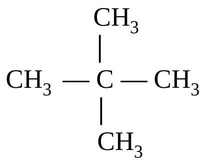
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

***n*-Pentane**



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

2-Methylbutane
(Isopentane)



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

2,2-Dimethylpropane
(Neopentane)

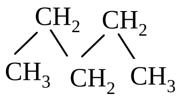
Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

Density: *The density of alkanes increases with the increase in molecular mass which increases with the increase in the number of carbon atoms.* All alkanes are lighter than water i.e. their density is less than 1.0 g/cm^3. The maximum density in the case of alkanes is 0.89 g cm^3. The lower density of alkanes than water is due to the absence of strong intermolecular attractions in alkanes.

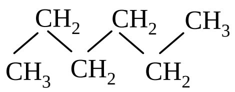
Boiling Point: *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. Thus, in the above example, isopentane and neopantane have a lower boiling point than pentane.

Melting Point: Similar to the boiling points, the melting points of alkanes also increase with the increase in their molecular mass, but there is no regular variation in melting point. The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (i.e. the packing) of the molecules in the crystal lattice.

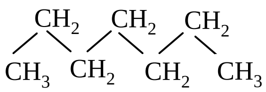
In alkanes, each carbon atom is sp^3 hybridized which results in a bond angle of $109^0 28'$. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the interaction between the alkane molecules, with odd number of carbon atoms, is less than the molecule with even number of carbon atoms, in which terminal methyl groups lie on the opposite sides.



***n*-Pentane**
(Carbon atoms = 5, m.p.142 K)



***n*-Hexane**
(Carbon atoms =6, m.p. = 179 K)



***n*-Heptane**
(carbon atoms = 7, m.p. = 183 K)

In the above structures, we find that alkanes containing even number of carbon atoms are more symmertical and can be more closely packed as compared with alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, due to which they have higher melting points. *Therefore, the alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms.*

26.1.3 Chemical Properties of Alkanes

1. Halogenation reactions: The chemical reactions in which a hydrogen atom of an alkane is replaced by a halogen atom are known as *halogenation*. Alkanes react with chlorine in the following way.

$$\underset{\textbf{Methane}}{CH_4} + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} \underset{\textbf{Chloromethane}}{CH_3Cl}$$

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Tetrachloromethane}}{CCl_4}$$

Chlorination of methane takes place via the **free radical mechanism**. When the reaction mixture is exposed to sunlight, chlorine molecules absorb energy from sunlight and get converted to free radicals i.e. chlorine atoms with an unpaired electron $(\dot{C}l)$. The chlorine radicals then combine with methane and form methyl radical $[\dot{C}H_3]$. The methyl radical further reacts with chlorine molecule and produces chloromethane. This reaction continuously takes place till it is stopped or the reactants completely react to form the products. The free radical mechanism involves the following three steps.

(i) **Chain Initiation Step:** It involves the formation of free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet} \qquad (h\nu = \text{energy of light})$$

(ii) **Chain Propagation Step :** The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \overset{\bullet}{C}l \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \overset{\bullet}{C}l$$

(iii) **Chain Termination Step :** In this step, free radicals combine with one another and the further reaction stops.

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}l \longrightarrow CH_3Cl$$

$$\overset{\bullet}{C}l + \overset{\bullet}{C}l \longrightarrow Cl_2$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3 - CH_3$$

The reactivity of halogens is in the order of $F_2 > Cl_2 > Br_2 > I_2$.

2. Oxidation: Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature.For example :

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \;+\; 890\text{ KJ mol}^{-1}$$

If the combustion is carried out in the presence of an insufficient supply of air or O_2, then *incomplete combustion takes place forming carbon monoxide* instead of carbon dioxide.

$$2C_2H_6 + 5O_2 \xrightarrow{\text{heat}} 4CO + 6H_2O$$

3. Cracking or Pyrolysis: At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873\text{ K}} CH_3CH = CH_2 + H_2$$

or $\qquad CH_2 = CH_2 + CH_4$

4. Isomerisation : *n*-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.

$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{AlCl_3 / HCl} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3$$

***n*-butane** **isobutane**

26.1.4 Uses of Alkanes

Alkanes are used as fuel gases, solvents, drycleaning agents, lubricants and in ointments (paraffin wax). Methane is used for illuminating and domestic fuel and also for the production of other organic compounds such as haloalkanes, methanol, formaldehyde and acetylene. Propane is used as a fuel, refrigerant and as raw material in the petrochemical industry. Butane and its isomer–isobutane, are the major constituents of LPG .

Intext Questions 26.1

1. List four important uses of hydrocarbons.

   ....

2. What is Grignard's reagent in a molecule?

   ....

3. What is an active hydrogen in a molecule?

   ....

4. What makes the physical properties of various hydrocarbons different?

   ....

5. Name two alkanes which are gases and two alkanes which are liquids at room temperature.

   ....

6. Name three isomers of pentane.

   ....

7. Which one has higher b.p. *n*-butane or *n*-pentane? Explain.

   ....

8. Write the balanced chemical equation for the complete combustion of propane.

   ....

26.2 Alkenes

These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called **olefines** (*olefiant* = oil forming).

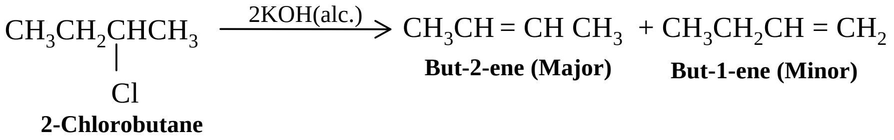
26.2.1 Methods of Preparation

In the laboratory, alkenes are generally prepared either from haloalkanes (alkyl halides) or alcohols.

1. From Haloalkanes: Halaoalkanes are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCl, HBr or HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called *dehydrohalogenation*.

$$CH_3 — CH_2 — Cl + KOH(alc.) \rightarrow CH_2 = CH_2 + KCl + H_2O$$

Chloroethane **Ethene**



$$\underset{\substack{|\\ Cl}}{CH_3CH_2CHCH_3} \xrightarrow{2KOH(alc.)} CH_3CH = CH\ CH_3 + CH_3CH_2CH = CH_2$$

2-Chlorobutane **But-2-ene (Major)** **But-1-ene (Minor)**

The major product is formed according to the Saytzeff's Rule.

Saytzeff's Rule : ***It states that when an alkyl halide reacts with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more substituted, will be the major product.*** In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the –C=C– group.

2. From Alcohols : Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as (i) Al_2O_3 or (ii) concentrated H_2SO_4.

$$\underset{\textbf{Ethanol}}{CH_3 - CH_2 - OH} \xrightarrow[623-633K]{Al_2O_3} \underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2O$$

$$\underset{\textbf{Ethanol}}{CH_3 - CH_2 - OH} \xrightarrow[433K]{conc.\ H_2SO_4} \underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2O$$

In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule.

26.2.2 Physical Properties of Alkenes

Some important physical properties of alkanes are as follows:

Physical State : Unbranched alkenes containing upto four carbon atoms are gases and containing five to sixteen carbon atoms are liquids while those with more than 16 carbon atoms are solids.

Boiling Points : The boiling points of alkenes increase with molecular mass as is shown in Table 26.1.

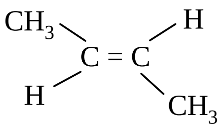
Table 26.1 : Boiling points of Alkenes

Alkene	Ethene	Propene	But-1-ene	Pent-1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

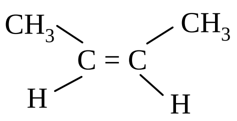
The increase in boiling point can be attributed to the van der Waals forces which increases with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

Melting Point : In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the ***cis*** and ***trans*** isomers have different melting points.

For example



***trans*-But-2-ene**
(m.p. 167 K)



***cis*-But-2-ene**
(m.p. = 134 K)

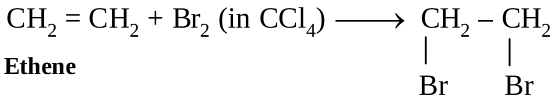
26.2.3 Chemical Properties of Alkenes

1. **Addition Reactions :** The chemical reactions in which a molecule adds to another molecule are called an *addition reaction*. These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

(i) **Addition of Hydrogen :** Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[573K]{Ni\ (Pt\ or\ Pd)} \underset{\textbf{Ethane}}{CH_3 - CH_3}$$

(ii) **Addition of Halogens :** Halogens on addition to alkenes, form 1,2-dihaloalkanes.



$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + Br_2\ (in\ CCl_4) \longrightarrow \underset{\textbf{1, 2-Dibromoethane}}{\underset{Br\qquad Br}{CH_2 - CH_2}}$$

As a result of this addition reaction, the reddish-brown colour of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

(iii) **Addition of Halogen Acids (HX) :** When halogen acids are added to alkenes , hydrogen adds to one carbon atom whereas halogen atom adds to the second carbon atom of the double bond.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} \quad + \quad HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3 - CH_2 - Br}$$

In case of unsymmetrical alkenes (which contain unequal number of H-atoms attached to the carbon atoms of the double bonds), the addition of HX takes place according to the **Markownikoff's rule. This rule states that in the addition of halogen acids to unsymmetrical alkenes, the halogen of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it.** In other words, hydrogen atom of HX goes to the carbon atom with more number of H-atoms attached to it.

$$\underset{\textbf{Propene}}{CH_3CH = CH_2} + HBr \longrightarrow \underset{\textbf{2-Bromopropane}}{CH_3CHBr\ CH_3}$$

If the addition of HBr is carried out in the presence of peroxides such as benzoyl peroxide, then the reaction takes place contrary to Markownikoff's rule. This is also known as **Anti Markownikoff's addition** or **peroxide effect**.

$$\underset{\textbf{Propene}}{CH_3CH = CH_2} + HBr \xrightarrow{\text{benzoyl peroxide}} \underset{\textbf{1 – Bromopropane}}{CH_3CH_2 - CH_2 - Br}$$

(iv) **Addition of Water :** Addition of water takes place in the presence of mineral acids like H_2SO_4.

$$CH_2 = CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3 - CH_2 - OH$$

Ethene **Ethanol**

(v) Addition of H_2SO_4

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow CH_3 - CH_2 - HSO_4$$

Ethene **Ethyl hydrogen sulphate**

(vi) Addition Polymerization : The process in which many molecules of an alkene add together to form a larger molecule is called **addition polymerization.**

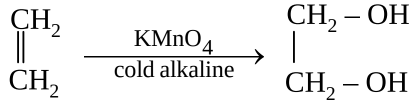
$$n\,(CH_2{=}CH_2) \xrightarrow[\text{heat, pressure}]{} \left(CH_2 - CH_2 \right)_n$$

Ethene **Polyethene**

2. Oxidation : The oxidation of alkenes can be done by using different oxidizing agents like $KMnO_4$, oxygen and ozone.

(i) Oxidation with $KMnO_4$

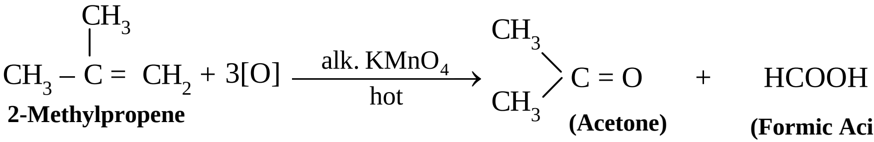
Alkenes are unsaturated hydrocarbons having Pi (®)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow[\text{cold alkaline}]{KMnO_4} \begin{matrix} CH_2 - OH \\ | \\ CH_2 - OH \end{matrix}$$

Ethene **Ethanediol**

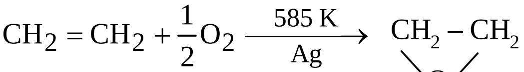
When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 + 3[O] \xrightarrow[\text{hot}]{\text{alk. } KMnO_4} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\!\!> C = O \quad + \quad HCOOH$$

2-Methylpropene **(Acetone)** **Propanone** **(Formic Acid)** **Methanoic acid**

(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:



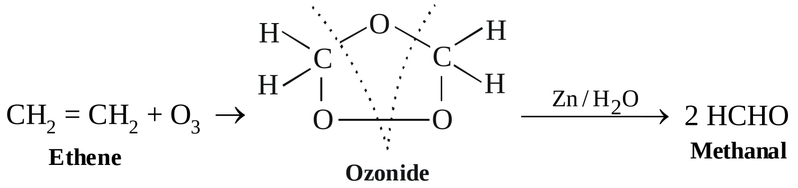
$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{Ag}]{585\text{ K}} \begin{matrix} CH_2 - CH_2 \\ \diagdown\ O\ \diagup \end{matrix}$$

Ethene **Epoxyethane**

(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called **combustion.**

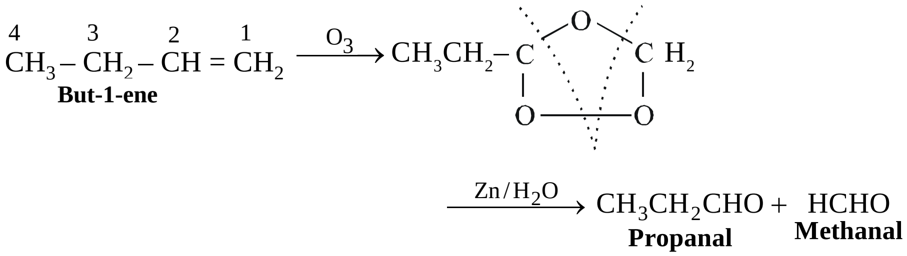
$$CH_2 = CH_2 + 3\,O_2 \xrightarrow{\text{heat}} 2\,CO_2 + 2\,H_2O \qquad \Delta H = -1411\text{ KJ mol}^{-1}$$

(iv) Oxidation with Ozone : Ozone adds to the alkene forming ozonide. The ozonide when further reacted with water in the presence of zinc dust, forms aldehydes or ketones, or both.

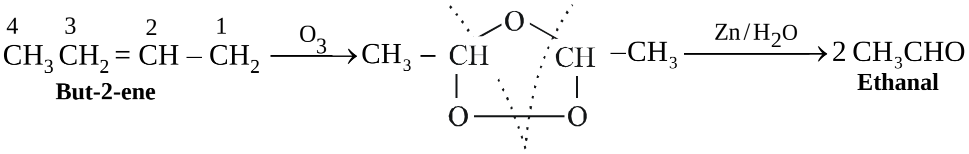


This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis.**

Ozonolysis can be used for the determination of the position of double bonds in alkenes by analysing the products formed i.e. aldehydes and ketones. This is explained below.



When but-1-ene is oxidized with ozone and the ozonide formed is hydrolysed, we get one mole of propanal and one mole of methanal, showing that the double bond is between carbon atom 1 and 2. Whereas but-2-ene on oxidation with ozone, followed by hydrolysis, gives two moles of ethanal, showing that the double bond is present between carbon atoms 2 and 3 as shown below.



26.2.4 Uses of Alkenes

Ethene is used for making mustard gas, which is a poisonous gas used in warfare. It is also used for artificial ripening of fruits, as a general anaesthetic and for producing other useful materials such as polythene, ethanal, ethylene glycol (antifreeze), ethylene oxide (fumigant) etc.

Intext Questions 26.2

1. Which one has higher boiling point*: cis* but-2-ene or *trans* but-2-ene?

....

2. Name the products formed when ethene is oxidized with cold alkaline solution of $KMnO_4$.

....

3. Write the conditions for hydrogenation of alkenes.

   ....

4. What happens when ethene reacts with oxygen at 575 K in presence of Ag?

   ....

26.3 Alkynes

These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$$\underset{\textbf{Ethyne}}{CH \equiv CH}, \quad \underset{\textbf{Propyne}}{CH_3 - C \equiv CH}, \quad \underset{\textbf{But-2-yne}}{CH_3 - C \equiv C - CH_3}$$

26.3.1 Preparation of Ethyne (Acetylene):

Some important methods for preparation of ethyne are explained below.

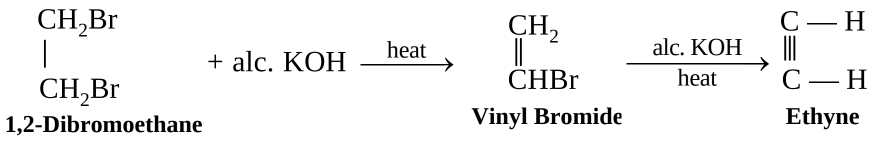
1. From Calcium Carbide: Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

$$\underset{\textbf{Calcium carbide}}{CaC_2} + \underset{\textbf{Water}}{2\,H_2O} \longrightarrow \underset{\textbf{Ethyne}}{H - C \equiv C - H} + Ca(OH)_2$$

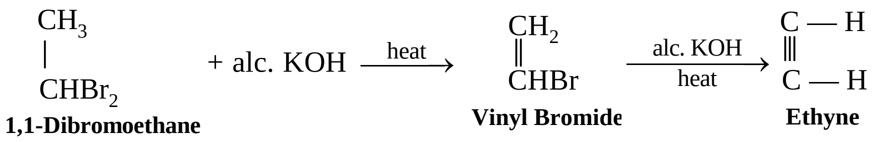
Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

2. Preparation of Ethyne from Dihaloalkanes

Ethyne can be prepared by refluxing *geminal* dihaloalkanes (having both halogens attached to the same carbon atom) or *vicinal* dihaloalkanes (having halogen atoms attached to the adjacent carbon atoms) with alcoholic solution of KOH.



$$\underset{\textbf{1,2-Dibromoethane}}{\begin{array}{c} CH_2Br \\ | \\ CH_2Br \end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\textbf{Vinyl Bromide}}{\begin{array}{c} CH_2 \\ \| \\ CHBr \end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\textbf{Ethyne}}{\begin{array}{c} C - H \\ ||| \\ C - H \end{array}}$$



$$\underset{\textbf{1,1-Dibromoethane}}{\begin{array}{c} CH_3 \\ | \\ CHBr_2 \end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\textbf{Vinyl Bromide}}{\begin{array}{c} CH_2 \\ \| \\ CHBr \end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\textbf{Ethyne}}{\begin{array}{c} C - H \\ ||| \\ C - H \end{array}}$$

3. Preparation of higher alkynes : Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R - C \equiv CH + Na \xrightarrow{\text{liq. } NH_3} R - C \equiv C^- Na^+$$

$$R - C \equiv C^- Na^+ + CH_3I \longrightarrow R - C \equiv C - CH_3 + NaI$$

26.3.2 Physical Properties of Alkynes

1. First three members of alkynes are gases, the next eight members are liquids and members having more than twelve carbon atoms are solids.
2. They are colourless and odourless, except ethyne which has a garlic odour.
3. The melting points, boiling points and densities of alkynes increase with the increasing molar mass. In alkynes, there are π(pi)-electrons due to which these molecules are slightly polar. So charge separation takes place in alkynes, and hence dipoles are formed. The presence of dipoles increases the inter molecular force of attraction, and hence the boiling points of alkynes are higher than those of the corresponding alkanes.
4. Alkynes are very slightly soluble in water and soluble in acetone.

26.3.3 Chemical Properties of Alkynes

1. Addition Reactions : Some of the addition reactions of alkynes are as follows.

(i) Addition of Hydrogen : Addition of hydrogen to alkynes takes place in the presence of a catalyst like Ni, Pt or Pd.

$$CH \equiv CH + H_2 \xrightarrow[573\text{ K}]{\text{Ni or Pt or Pd}} CH_2 = CH_2 \xrightarrow{H_2 + \text{Ni or Pt or Pd}} CH_3 - CH_3$$

(ii) Addition of Halogens : When halogens are added to alkynes, they form 1,2-dihaloalkenes and 1,1,2,2-tetrahaloalkanes.

$$CH \equiv CH \xrightarrow{Br_2 \text{ in } CCl_4} CHBr = CHBr \xrightarrow{Br_2 \text{ in } CCl_4} CHBr_2 - CHBr_2$$

Ethyne **1,2-Dibromoethene** **1,1,2,2-Tetrabromoethane**

(iii) Addition of Halogen Acids (HX) : Addition of HBr to ethyne is as follows :

$$CH \equiv CH \xrightarrow{HBr} CH_2 = CHBr \xrightarrow{HBr} CH_3 - CHBr_2$$

Ethyne **Bromoethene** **1,1–Dibromoethane**

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4 and in the presence of Hg^{2+} as the catalyst.

$$CH \equiv CH + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} [CH_2 = CHOH] \xrightleftharpoons{\text{Rearrangement}} CH_3CHO$$

Ethyne **Vinyl Alcohol (Unstable)** **Ethanal**

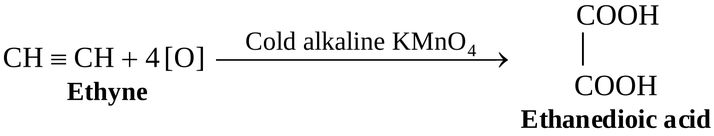
(v) Addition of H_2SO_4: Conc. H_2SO_4 adds to ethyne as shown below.

$$CH \equiv CH \xrightarrow{\text{conc. } H_2SO_4} CH_2 = CHHSO_4 \xrightarrow{H_2SO_4} CH_3 - CH\ (HSO_4)_2$$

Vinyl hydrogen sulphate **Ethylidene hydrogen sulphate**

2. Oxidation : Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

(i) **Oxidation with $KMnO_4$**



$$CH \equiv CH + 4[O] \xrightarrow{\text{Cold alkaline } KMnO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Ethyne **Ethanedioic acid**

The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

$$\equiv C - R' \xrightarrow[\text{heat}]{KMnO_4 + KOH} RCOOH + R'\,COOH$$

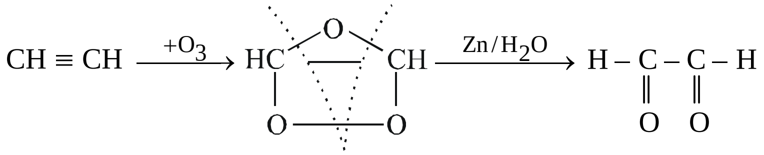
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH \equiv CH + 4\,[O] \xrightarrow[\text{heat}]{KMnO_4 + KOH} (COOH)_2 \xrightarrow[\text{Heat}]{[O]} 2\,CO_2 + H_2O$$

Combustion : Combustion of ethyne in excess of oxygen or air gives carbon dioxide and water as shown below :

$$2\,C_2H_2 + 5\,O_2 \xrightarrow{\text{heat}} 4\,CO_2 + 2\,H_2O \quad \Delta H = -1300 \text{ KJ mol}^{-1}$$

Ozonolysis : On ozonolysis, alkynes give dicarbonyl compounds at the position of C≡C without breaking the chain of carbon atoms as shown below :



3. **Formation of Acetylides :** Ethyne forms precipitates of copper and silver acetylides when passed through ammonical solution of cuprous chloride and ammonical silver nitrate, respectively.

$$CH \equiv CH + 2Cu(NH_3)_2 \longrightarrow CuC \equiv CCu + 2\,NH_4^+ + 2\,NH_3$$

Cuprous acetylide (red)

$$CH \equiv CH + 2Ag(NH_3)_2 \longrightarrow AgC \equiv CAg + 2\,NH_4^+ + 2\,NH_3$$

Silver acetylide (white)

26.3.4 Acidic Nature of Ethyne

The acidic nature of hydrocarbons can be determined with the help of the percentage (%) of *s*-character of the hydrocarbon. The greater the percentage of *s*-character of a hydrocarbon, the more will be its acidic nature.

Table 26.2 : % *s*-Character of hyrid orbitals in Hydrocarbons

Hydrocarbon	**Type of hybridization**	**(%) s-character**
Alkanes	sp^3	25%
Alkenes	sp^2	33.3%
Alkynes	sp	50%

As alkynes have 50% *s*- character, they are the most acidic in nature. An *sp*-hybridized carbon atom is more electronegative than sp^2 or sp^3 carbon atoms. Due to greater electronegativity of *sp* hybridized carbon atom in ethyne, hydrogen atom is less tightly held by the carbon and hence, it can be removed as a proton (H^+) by a strong base like sodium metal and sodamide. **The following reactions of ethyne with sodium and sodamide confirm its acidic nature.** In these reactions, disodium acetylide is formed.

$$H - C \equiv C - H + 2\ Na \xrightarrow{Heat} Na - C \equiv C - Na + H_2$$

Ethyne (Acetylene) → **Disodium Acetylide**

$$H - C \equiv C - H + 2\ NaNH_2 \xrightarrow{Heat} Na - C \equiv C - Na + 2\ NH_3$$

Ethyne **Sodamide** → **Disodium Acetylide**

26.3.5 Uses of Alkynes

Ethyne (acetylene) is used for producing oxyacetylene flame (2800ºC) which is used for for welding and cutting of iron and steel. It is also used for artificial ripening of fruits and vegetables. It also finds use in the production of a number of other organic compounds such as ethanal, ethanoic acid, ethanol, synthetic rubbers and synthetic fibre *orlon*.

26.3.6 Distinction Between Alkanes, Alkenes and Alkynes

The folloiwng table shows different tests for distinction between alkanes, alkenes and alkynes :

Table 26.3 : Tests for identification of alkanes, alkenes and alkynes

S.No	Test	Alkanes	Alkenes	Alkynes
1.	Add bromine dissolved in carbon tetrachloride.	No change	Reddish brown colour of Br_2 is discharged	Reddish brown colour of Br_2 is discharged
2.	Add alkaline solution of $KMnO_4$ (Baeyer's reagent)	No change	Purple colour of $KMnO_4$ is discharged	Purple colour of $KMnO_4$ is discharged
3.	Add ammonical solution of silver nitrate	No change	No change	White ppt. of silver acetylide is formed
4.	Add ammonical solution of cuprous chloride (Cu_2Cl_2)	No change	No change	Red ppt. of cuprous acetylide is formed

Intext Questions 26.3

1. How is ethyne prepared from calcium carbide?

   ....

2. Give one reaction to confirm the acidic nature of ethyne.

   ....

3. What is the percentage of *s*-character in ethane, ethene and ethyne?

....

26.4 Aromatic Hydrocarbons

Till now, we have explained various methods of preparation of aliphatic hydrocarbons. Now, we shall deal with an aromatic hydrocarbon (benzene) in detail. It is one of the major components obtained by the destructive distillation of coal as shown in Fig. 26.1

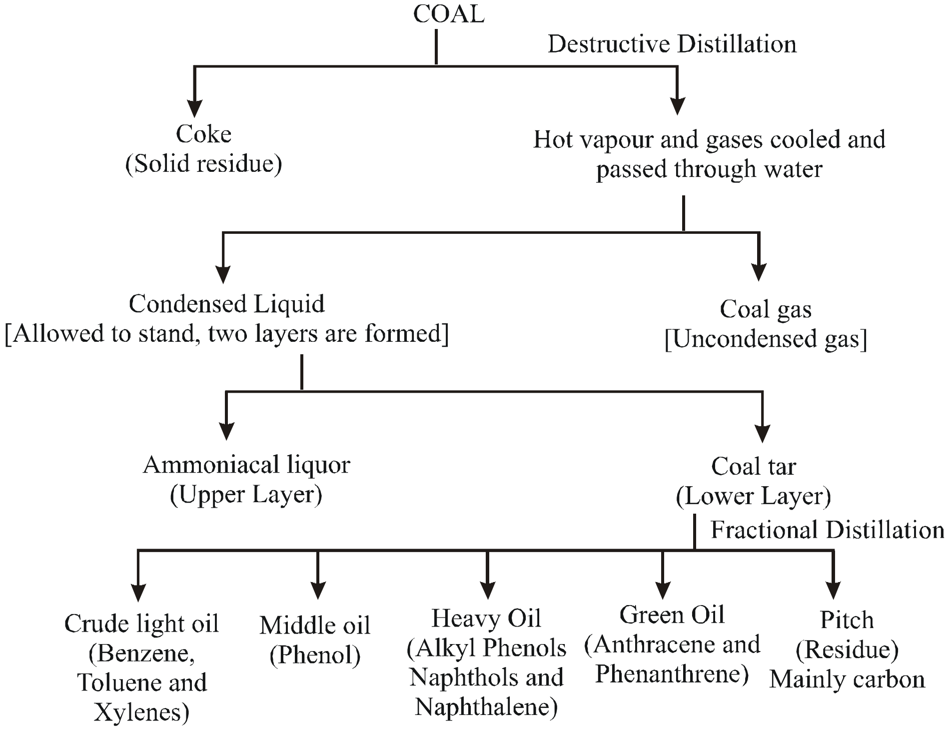


Fig. 26.1 : *Destructive Distillation of coal*

26.4.1 Structure of Benzene

The molecular formula of benzene is C_6H_6 which indicates that benzene is an unsaturated hydrocarbon. The unsaturation in benzene can be verified by the following reactions.

(i) Benzene undergoes the addition of H_2 in the presence of Ni or Pt as catalyst.

$$\underset{\textbf{Benzene}}{C_6H_6} + 3H_2 \xrightarrow{\text{Ni or Pt}} \underset{\textbf{Cyclohexane}}{C_6H_{12}}$$

(ii) Benzene undergoes the addition of chlorine in the presence of sunlight.

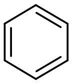
$$\underset{\textbf{Benzene}}{C_6H_6} + 3\,Cl_2 \xrightarrow{h\nu} \underset{\textbf{Benzene hexachloride (B.H.C.)}}{C_6H_6Cl_6}$$

Benzene does not respond to the tests of unsaturation which are shown by alkenes and alkynes i.e., both the alkenes and the alkynes decolourize bromine water and alkaline solution of potassium permanganate (Bayer's Reagent). However, benzene undergoes substitution reactions.

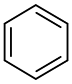
e.g. $C_6H_6 + Br_2 \xrightarrow{\text{Fe or FeCl}_3} C_6H_5Br + HBr$

Benzene **Bromobenzene**

Kekule Structure : A ring structure for benzene was proposed by Kekule in 1865. According to him, six carbon atoms are joined to each other by alternate single and double bonds to form a hexagon ring. As the proposed structure of benzene has three double bonds, so its properties should resemble with the properties of alkenes. But the chemical properties of benzene are different from alkenes.

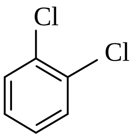


or

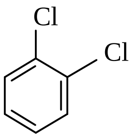


As Kekule's structure contains three single bonds and three double bonds, one may expect that in benzene there should be two different bond lengths i.e. 154 pm for C-C single bond and 134 pm for C=C double bond. But the experimental studies show that benzene is regular hexagon with an angle of 120^0 and all the carbon-carbon bond lengths are equal i.e. 139 pm.

If Kekule's structure is to be taken as a true structure, then benzene should form only one monosubstitution product and two ortho distubstitution products, shown below as (a) and (b).

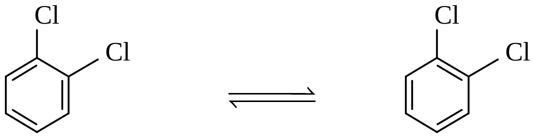


(a)



(b)

In structure (a), the two halogen atoms are on the doubly bonded carbon atoms, whereas in structure (b), the two halogen atoms are on singly bonded carbon atoms. As per the Kekule's structure these two isomers (a and b) should exist and show different properties. But, in reality, only one ortho disubstituted product exists. In order to explain this, Kekule proposed a dynamic equilibrium between the two structures.



Kekule's structure does not explain the stability of benzene and its some unusual reactions. Resonance can explain the unusual behaviour of benzene. Let us now study about resonance.

Resonance : ***The phenomenon by virtue of which a single molecule can be represented in two or more structures is called resonance.*** The actual structure is the resonance hybrid of all the canonical or resonating structure. (see lesson 25)

Heat of hydrogenation data provides proof for resonance stabalization in benzene. **The heat of hydrogenation is the amount of heat liberated when hydrogen is added to one mole of an unsaturated compound in the presence of a catalyst.**

$$\text{Cyclohexene} + H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 119.5\ \text{KJ mol}^{-1}$$

(One – C = C– bond)

If the three double bonds in benzene do not interact, then it should behave like cyclohexatriene and the amount of heat liberated on adding there molecules of hydrogen should be 358.5 KJ mol^{-1}. But, the actual heat of hydrogenation of benzene is 208.2 KJ mol^{-1}.

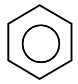
$$\text{Benzene} + 3H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 208.2\ \text{KJ mol}^{-1}$$

(Three – C = C– bond)

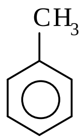
This difference of (358.5 – 208.2) 150.3 KJ mol^{-1} in the heat of hydrogenation is the measure of stability of benzene. Benzene acquires stability due to resonance and hence, this energy is called resonance energy of benzene.

26.4.2 Physical Properties of Aromatic Hydrocarbons

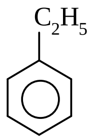
1. Benzene and its homologues are colourless liquids having a characteristic odour.
2. They are immiscible in water but are miscible in all proportions with organic solvents such as alcohol, ether, petrol, etc. They dissolve fats and many other organic substances.
3. Most of the aromatic hydrocarbons are lighter than water.
4. Their boiling points show a gradual increase with increasing molecular mass e.g. benzene (b.p. 353 K), toluene (b.p. 383 K) and ethylbenzene (b.p. 409 K) and so on.



Benzene
(b.p. 353 K)



Toluene
(b.p. 383 K)

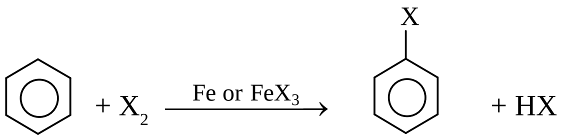


Ethylbenzane
(b.p. 409 K)

26.4.3 Chemical Properties of Aromatic Hydrocarbons

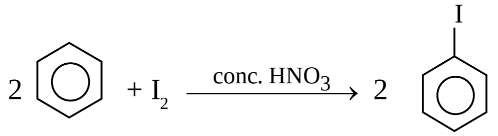
Aromatic hydrocarbons generally undergo electrophilic substitution reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile. Such reactions are discussed below in detail taking benzene as an example.

(i) Halogenation : The reaction in which a hydrogen atom of benzene is replaced by a halogen atom is called halogenation of benzene. Halogenation takes place in the presence of iron, or ferric halides (FeX_3, where X = Cl or Br).



Halobenzene

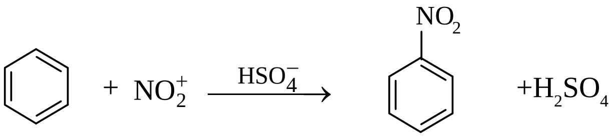
In case of iodination the HI formed can reduce iodobenzene back to be benzene which is prevented by carrying out this reaction in the presence of HNO_3 or HIO_3. These acids react with HI as soon as it is formed.



Iodobenzene

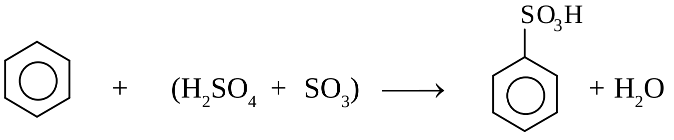
(ii) **Nitration :** The chemical reaction in which a hydrogen atom of benzene ring is replaced by $-NO_2$ group, is called nitration. It is carried out in the presence of nitrating mixture, i.e. a mixture of conc. HNO_3 and conc. H_2SO_4. Nitronium ion (NO_2^+) so formed acts as an electrophile.

$$2\,H_2SO_4 + HNO_3 \longrightarrow 2\,HSO_4^- + NO_2^+ + H_3O^+$$



Nitrobenzene

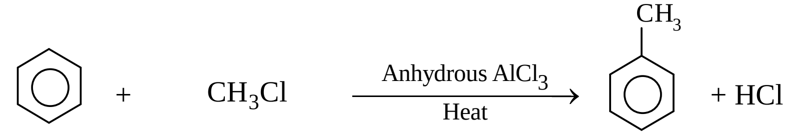
(iii) **Sulphonation :** The chemical reaction in which the hydrogen atom of benzene is replaced by $-SO_3H$ group when benzene is heated with fuming sulphuric acid (oleum), is called sulphonation.



Fuming sulphuric acid **Benzenesulphonic acid**

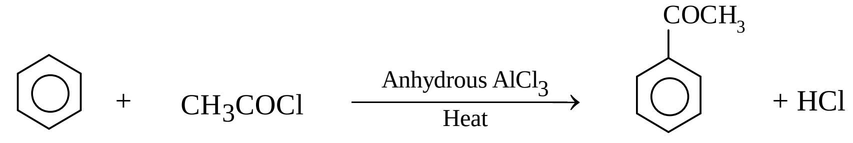
(iv) **Friedel–Craft's Reactions :** In Friedel-Craft's reaction, benzene is heated either with alkyl halide **(alkylation)** or acyl halide **(acylation)** in the presence of a catalyst (anhydrous $AlCl_3$). The products formed are alkyl or acyl derivatives of benzene.

Alkylation



Benzene **Chloromethane** **Toluene**

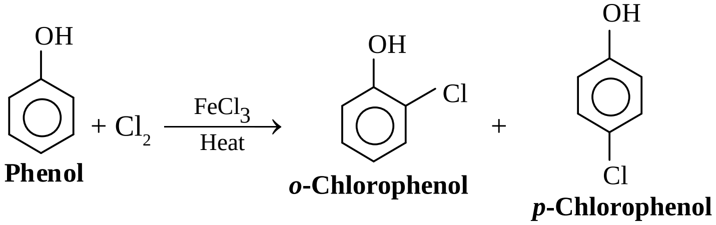
Acylation



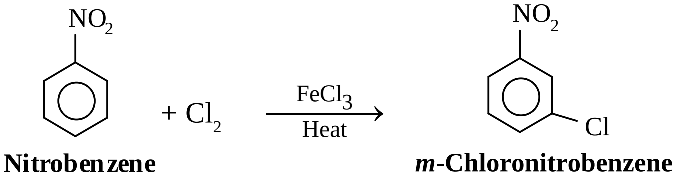
Benzene **acetyl chloride** **Acetophenone**

26.4.4 Directive Influence of Functional Groups

In case of substituted aromatic compounds, the functional group(s) already present directs the next incoming group to a particular position in the aromatic ring.. It is called directive influence of the group already attached to the benzene ring. For example, phenol on chlorination gives a mixture of *ortho* – chlorophenol and *para*– chlorophenol as – OH groups is an *ortho* and *para* directing group.



In case of nitrobenzene, we find that $-NO_2$ group is a *meta* directing group and hence, the product obtained on chlorination is *meta*-chloronitrobenzene.



26.4.5 Uses of Aromatic Hydrocarbons

Benzene is used as a solvent for several organic compounds and thus, acts as a medium for carrying out synthetic reactions. It is the basic aromatic hydrocarbon and can be converted to other organic compounds by carrying out substitution in the benzene ring. **Toluene,** a higher homologue of the benzene, finds its uses for dry-cleaning, as a solvent, and as a starting material for the manufacture of dyes, drugs, explosive (trinitrotoluene, T.N.T.), benzaldehyde, benzoic acid etc.

Intext Questions 26.4

1. What is the value of resonance energy of benzene?

   ....

2. Name the product formed when :
   (i) benzene reacts with chlorine in the presence of light.

   ....

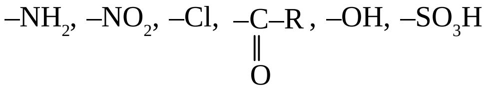
   (ii) phenol reacts with chlorine in the presence of $FeCl_3$.

   ....

   (iii) nitrobenzene reacts with chlorine in the presence of $FeCl_3$.

   ....

3. Classify the following into *o*-and *p*- or *m*-directing groups :



$-NH_2$, $-NO_2$, $-Cl$, $-\underset{\underset{O}{\|}}{C}-R$, $-OH$, $-SO_3H$

....

What You Have Learnt

- Alkanes can be prepared by (i) the reduction of haloalkanes, (ii) action of water or alcohol on Grignard's reagent, (iii) Wurtz reaction and (iv) hydrogenation of unsaturated hydrocarbons.
- Physical properties of hydrocarbons depend on the intermolecular forces of attraction. which in turn depend upon the shapes of molecules and their surface area.
- The melting points of hydrocarbons depends upon the symmetry of the molecules i.e. hydrocarbons with even number of carbon atoms are more symmetrical and have higher melting points.
- Alkenes can be prepared by dehydrohalogenation of alkyl halides and by dehydration of alcohols.
- Alkenes and alkynes undergo addition reactions e.g. addition of hydrogen, halogens, halogen acids, water, sulphuric acid etc. due to the presence of carbon-carbon double or triple bonds.
- Addition of halogen acids and other unsymmetrical reagents to unsymmetrical alkenes and alkynes takes place according to the Markownikoff's rule.
- Alkenes undergo polymerization on heating under pressure.
- All hydrocarbons (saturated as well as unsaturated) form CO_2 and H_2O on combustion and liberate energy.
- An alkaline solution of $KMnO_4$ can oxidize alkenes and alkynes forming different products such as carboxylic acids, aldehydes and/or ketones and carbon dioxide.
- Ozone can oxidize unsaturated hydrocarbons (alkenes and alkynes) forming ozonides which when further reacted with water in the presence of zinc dust either form aldehydes or ketones or both.
- Reaction of ozone with alkenes can be used to determine the position of double bond.
- Ethyne can be prepared by the action of water on calcium carbide and by dehydrogenation of dihaloalkanes.
- Alkynes are acidic in nature due to *sp*-hybridization of carbon atoms. Because *sp* hybridized carbon atoms are more electronegative than sp^2 and sp^3, and the bond between C—H is weakened. Hence, hydrogen atoms in alkynes can be replaced by certain metal atoms.
- Alkanes, alkenes and alkynes can be distinguished by using:
  a) Br_2 dissolved in carbon tetrachloride. b) Ammoniacal solution of $AgNO_3$
  c) Ammoniacal solution of Cu_2Cl_2 d) Alkaline solution of $KMnO_4$

- Benzene is obtained by destructive distillation of coal.
- A ring structure of benzene was suggested by Kekule. Actual structure of benzene is the resonance hybrid of the canonical structures.
- Aromatic hydrocarbons undergo substitution reactions i.e. the reactions in which hydrogen atom of hydrocarbons is replaced by another atom or group of atoms. Halogenation, sulphonation, nitration and Friedel Craft's reaction are substitution reactions of benzene.
- The position of second substituent on a benzene ring depends upon the nature of the group already present.

Terminal Exercise

1. What happens when : (Write chemical equations)
   (i) Iodoethane is heated with HI in the presence of red phosphorus.
   (ii) 2-Chlorobutane reacts with sodium metal.
   (iii) Ethyl magnesium bromide is reacted with methyl alcohol (methanol).
   (iv) 2-Chloropropane reacts with alcoholic solution of KOH.
   (v) 1,1-Dichloroethane reacts with alcoholic solution of KOH.

2. Give reasons for the following :
   (i) The boiling point of neopentane is less than that of n-pentane.
   (ii) Stability of benzene ring
   (iii) Boiling points of hydrocarbons decrease with the increase in branching.

3. How will you prepare the following?
   (i) Ethane from ethene
   (ii) Ethene from ethanol
   (iii) Cyclohexane from benzene
   (iv) Methane from sodium acetate
   (v) Butane from bromoethane

4. What happens when (write balanced chemical equations):
   (i) Hydrochloric acid is added to ethene.
   (ii) Hydrobromic acid (HBr) is added to propene in the presence of benzoyl peroxide.
   (iii) Benzene reacts with chloromethane in the presence of anhydrous$AlCl_3$.
   (iv) Br_2 is added to ethyne.
   (v) Methane is oxidized with oxygen in the presence of copper at 475K and a high pressure of 120 atm.

5. How are the following conversions carried out?
   (i) Ethyne to ethane
   (ii) Benzene to nitrobenzene
   (iii) Ethyl alcohol (ethanol) to ethene

(iv) Ethyne to ethanedioic acid

(v) Benzene to *o*-nitrochlorobenzene.

6. You are provided with three gas jars containing ethane, ethene and ethyne. Give the suitable chemical tests to identify the three hydrocarbons.

7. What is ozonolysis? How is it used to determine the position of a double bond?

8. Give reasons for the following :

   (i) Alkanes do not undergo addition reactions like alkenes and alkynes.

   (ii) Ethyne is more acidic than ethane.

   (iii) Ethene undergoes polymerization but not ethane.

   (iv) Benzene undergoes electrophilic substitution reactions.

Answers to Intext Questions

26.1

1. They are used as fuels and to prepare detergents, dyes, drugs, explosives etc. Hydrocarbons are used to prepare some important organic compounds like alcohols, aldehydes, carboxylic acids etc.

2. The alkyl magnesium halides (R-MgX) are called Grignard's reagent.

3. Easily replaceable hydrogen present in a molecule is called active hydrogen.

4. The physical properties of hydrocarbons differ from one another due to difference in molecular mass, surface area, intermolecular force of attraction.

5. Methane and ethane are gases, pentane and hexane are liquids.

6. Three isomers of pentane are : *n*-pentane, isopentane and neopentane.

7. *n*-pentane has higher boiling point than n-butane.

8. $C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$

26.2

1. *Trans*-2-butene has higher boiling point than *cis*-isomer.

2. Ethane-1, 2-diol

3. Hydrogen in presence of catalist Ni, Pt or Pd

4. Epoxyethane is produced.

26.3

1. Calcium carbide is reacted with water to prepare ethyne.

   $CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

2. Reaction with sodium metal confirms the acidic nature of ethyne.

$$\underset{\textbf{Ethyne}}{H - C \equiv C - H} \quad + \quad 2\,Na \longrightarrow \underset{\textbf{Disodium acetylide}}{Na - C \equiv C - Na} + H_2$$

3. The *s*-character in : Ethane = 25%,
Ethene = 33%,
Ethyne = 50%

26.4

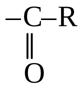
1. The resonance energy of benzene is 150.3 KJ mol^{-1}.

2. (i) Benzene hexachloride (BHC).

   (ii) *o*-Chlorophenol and *p*-chlorophenol.

   (iii) *m*-Chloronitrobenzene.

3. *o* – and *p* – directing groups : $-NH_2$, –Cl, – OH

   m-directing groups : NO_2,  $-\underset{\underset{O}{\|}}{C}-R$, – SO_3H