

Organic chemistry

Organic chemistry is the chemistry of the compounds of carbon. The misleading name "organic" is a relic of the days when chemical compounds were divided into two classes, inorganic and organic, depending upon where they had come from. Inorganic compounds were those obtained from minerals organic compounds were those obtained from vegetable or animal sources, that is, from material produced by living organisms. indeed, until about 1850 many chemists believed that organic compounds must have their origin in living organisms, and consequently could never be synthesized from inorganic material. These compounds from organic sources had this in common: they all contained the element carbon. Even after it had become clear that these compounds did not have to come from living sources but could be made in the laboratory, it was convenient to keep the name organic to describe them and compounds like them. The division

between inorganic and organic compounds has been retained to this day. Today, although many compounds of carbon are still most conveniently isolated from plant and animal sources, most of them are synthesized. They are sometime synthesized from inorganic substances like carbonates or cyanides, but more often from other organic compounds. There are two large reservoirs of organic material from which simple organic compounds are obtained : petroleum and coal. (Both of these are "organic " in the-old sense being products of the decay of plants and animals.) These simple compounds are used as building blocks from which larger and more complicated compounds can be made. We recognize petroleum and coal as the fossil fuels. laid down over millennia and non-renewable. They-particularly petroleum are being consumed at an alarming rate to meet. our constantly increasing demands for power.

Today, less than ten percent of the petroleum used goes into making chemicals; most of it is simply burned to supply energy . The number of compounds that contain carbon is many times

greater than the number of compounds that do not contain carbon. These organic compounds have been divided into families, which generally have no counterparts among the inorganic compounds. organic molecules containing thousands of atoms are known, and the arrangement of atoms in even relatively small molecules can be very complicated. one of the major problems in organic chemistry is to find out how the atoms are arranged in molecules, that is, to determine the structures of compounds. There are many ways in which these complicated molecules can break apart, or rearrange themselves, to form new molecules; there are many ways in which atoms can be added to these molecules, or new atoms substituted for old ones. Much of organic chemistry is devoted to finding out what these reactions are, how they take place, and how they can be used to synthesize compounds we want. organic chemistry is fundamental to biology and medicine. Aside from water, living organisms are made up chiefly of organic compounds; the molecules of molecular biology are organic molecules. Biology , on the molecular level is organic chemistry .

The structural theory

The structural theory is the framework of ideas about how atoms are put together to make molecules. The structural theory has to do with the order in which atoms are attached to each other, and with the electrons that hold them together. It has to do with the shapes and size of the molecules that these atoms form, and with the way that electrons are distributed over them.

Element and Compounds- Atom and molecules

Element are the fundamental building units of substance .they are composed of tiny particles called atom .

Atom are smallest particles of an element that retains the properties of the element .

Atoms are composed of a positively charged nucleus that consist of protons (charge = +1 , mass = 1) and neutrons

(charge = 0 , mass = 1) the nucleus is surrounded by negatively charged electrons that have negligible mass .

Elements combine to form compounds . A molecule is the smallest particle of compound that retains the properties of compound , atoms bond to one another to form a molecule .

Atomic orbitals

The space electrons occupy around an atomic nucleus is described by **atomic orbitals** , the most common orbitals in organic chemistry are **s- orbitals** spherical orbitals with the atomic nucleus located in the center , and dumbbell shaped **p-orbitals** in which the nucleus is between the lobes .

Filling Atomic Orbitals

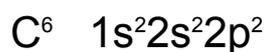
Orbitals exist in energy levels or shells an atomic orbital an occupied by 0 , 1 , 2 electrons atomic orbitals are filled according to the *Aufbau principle* beginning with the lowest energy orbitals and proceeding to higher energy ones .

The electron configuration of an atom is described by the orbitals occupied in each shell and the number of electrons in each orbitals .

Electron configuration and periodic table

The periodic of elements is organized according to electron configuration . Elements are placed in *periods* that related to

the outermost shell of electrons and in groups that are related to the number of electrons and in **groups** that are related to the number of electrons in the outer shell .



Both outer shell have four electrons (group 4)



1S

2S 2P

3S 3P 3d

4S 4P 4d 4f

5S 5P 5d 5f

6S 6p 6d

7S 7P

1S 2S 2P 3S 3P 4S 3d 4P 5S 4f 5d 6p 7S

Bonding in organic compounds

Ionic bonding involves the complete transfer of electrons between two atoms of widely different in electronegativities, charge (one positive from loss of electrons and one negative from the gain of electrons) both of which usually have a stable octet outer shell ,the ionic bond results from the attraction between positive cation and negative anion .

Electronegativity is define as the attraction of an atom for its outer shell electrons . Electronegative elements have a strong attraction and form anions in chemical reactions .

Covalent bond involve the sharing of electron pairs between atoms of similar electronegativities ,in most cases one or both atoms obtain a stable octet outer shell of electrons .

Polar covalent bonds A polar covalent is composed of atoms with similar but not equal electronegativities , The more electronegative atom is partially negative and the other is partially positive .

Hybrid orbitals: sp

Let us next consider beryllium chloride, BeCl₂.

Be⁴ 1S² 2S² 2P

Beryllium has no unpaired electrons. How are we to account for its combining with two chlorine atoms? Bond formation is an energy-releasing (stabilizing) process, and the tendency is to form bonds- and as many as possible even if this results in bond orbitals that bear little resemblance to the atomic orbitals we have talked about. If our method of mental molecule-building is to be applied here, it must be modified. we must invent an

imaginary kind of beryllium atom , one that is about to become bonded to two chlorine atoms ..

Hybrid orbitals: sp^2

Next let us look at boron trifluoride $B-F_3$.

Boron has only one unpaired electron , which occupies a 2p orbital . For three bonds we need three unpaired electrons, and so we promote one of the 2S electrons to a 2p orbital:

B^5 1S 2S 2P

SP^2 hybridization

1S 2S 2P

Hybrid orbitals: SP^3

Now, let us turn to one of the simplest of organic molecules, Methane CH_4 . Carbon has an unpaired electron in each of the two p orbitals, and on this basis might be expected to form a compound CH_2 . (It does, but CH_2 is a highly reactive molecule

whose properties center about the need to provide carbon with two more bonds.) Again, we see the tendency to form as many bonds as possible: in 'this case, to combine with four hydrogen atoms' To provide four unpaired electrons, we promote one of the $2s$ electrons to the empty p orbital:

Unshared pairs of electrons

Two familiar compounds, ammonia (NH_3) and water (H_2O), show how *unshared pairs of electrons* can affect molecular structure.

In ammonia, nitrogen resembles the carbon of methane hybridized, but has only three unpaired electrons; they occupy three of the sp^3 orbitals. Overlap of each of these orbitals with the s orbital of a hydrogen atom results in ammonia. The fourth sp^3 orbital of nitrogen contains a pair of electrons.

Bond dissociation energy. Homolysis and Heterolysis

We have seen that energy is liberated when atoms combine to form a molecule. For a molecule to break into atoms, an equivalent amount of energy must be consumed. *The amount of energy consumed or liberated when a bond is broken or formed is known as the **bond dissociation energy**, D.* It is characteristic of the particular bond. lists bond dissociation energies that have been measured for a number of bonds. As can be seen, they vary widely, from weak bonds like I- I (36 kcal/mol) to very strong bonds like H-F (136 kcal/mol). Although the accepted values may change as experimental methods improve, certain trends are clear.

Homolytic bond dissociation energy **IES**, K Cal /mol

**A : B → A. + B. AH = Homolytic bond dissociation energy or
D (A-B)**

H-H 104 , CH3-H 104

H-F 136	F-F 38	CH₃-F 108
H-Cl 103	Cl-Cl 58	CH₃-Cl 84
H-Br 88	Br-Br 46	CH₃-Br 70
H-I 71	I-I 36	CH₃-I 56

A:B → **A.+B.** Homolysis: *one' electron to each fragment*

A:B → **A + :B** Heterolysis : *both electrons to one fragment*

Hydrocarbons

Certain organic compounds contain only two elements, hydrogen and carbon, and hence are known as hydrocarbons. On the basis of structure, hydrocarbons are divided into two main classes, aliphatic and aromatic . Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (cycloalkanes, etc.). We shall take up these families in the order give

Hydrocarbons

Aliphatic

Aromatic

Alkanes , Alkenes , Alkynes

aliphatic Cyclic

The simplest member of the alkane family and, indeed, one of the simplest of all organic compounds is methane, CH_4 . We shall study this single compound at some length, since most of what we learn about it can be carried over with minor.

modifications to any alkane.

Structure of methane

As we discussed in the previous part , each of the four hydrogen atoms is bonded to the carbon atom by a covalent bond, that is, by the sharing

of a pair of electrons. When carbon is bonded to four other atoms, its bonding orbitals (sp^3 orbitals, formed by the mixing of one s and three p orbitals) are directed to the corners of a tetrahedron. This tetrahedral arrangement is the one that permits the orbitals to be as far apart as possible. For each of these orbitals to overlap most effectively the spherical s orbital of a hydrogen atom, and thus to form the strongest bond, each hydrogen nucleus must be located at a corner of this tetrahedral

Physical properties

- 1- the molecule itself is non-polar.
- 2- Melting point (-183°), boiling point (-161°).

3- Methane is colorless and, when liquefied, is less dense than water (sp.gr. 0.4).

4- In agreement with the rule of thumb that ("like dissolves like," it is only slightly soluble in water, but very soluble in organic liquids such as gasoline, ether, and alcohol. In its physical properties methane sets the pattern for the other members of the alkane family.

Reactions

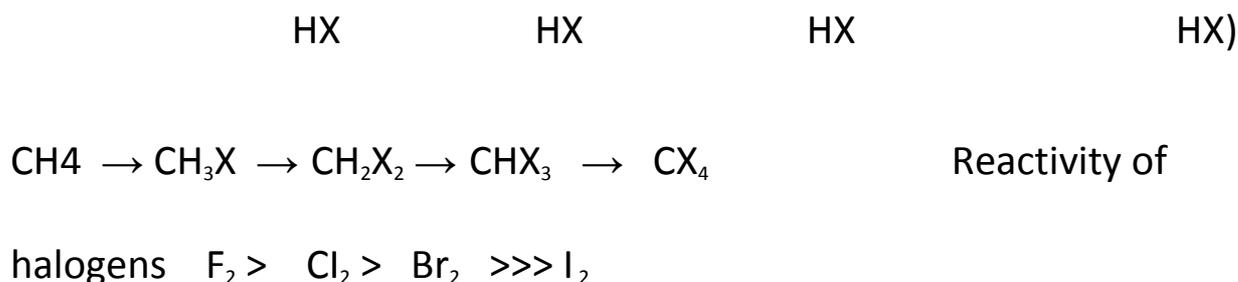
Typically, it reacts only with highly reactive substances or under very vigorous conditions, which, as we shall see, amounts the same thing. At this point we shall take up only its oxidation: by oxygen, by halogens, and even by water.

REACTIONS OF METHANE

1. Oxidation



2. Halogenation



Burning of hydrocarbons takes place only at high temperatures, as provided, for example, by a flame or a spark. Once started, however, the reaction gives off heat which is often sufficient to maintain the high temperature and to permit burning to continue. The quantity of heat evolved when one mole of a hydrocarbon is burned to carbon dioxide and water is called (the heat of combustion; for methane its value is 213 kcal.

Chlorination: a substitution reaction

Under the influence of ultraviolet light or at a temperature of 250-400 a

mixture of the two gases, methane and chlorine, reacts vigorously to yield hydrogen chloride and a compound of formula CH_3Cl . We say that methane has undergone chlorination, and we call the product, CH_3Cl , chloromethane or methyl chloride ($\text{CH}_3 = \text{methyl}$).

Chlorination is a typical example of a broad class of organic reactions known as substitution. A chlorine atom has been substituted for a hydrogen atom of methane, and the hydrogen atom thus replaced is found combined with a second atom of chlorine.

Ethane

Structure of ethane

Next in size after methane is ethane, C_2H_6 . If we connect the atoms of this molecule by covalent bonds, following the rule of one bond (one

pair of electron for each hydrogen and four bonds (four pairs of electrons) for each carbon, we arrive at the structure

Each carbon is bonded to three hydrogens and to the other carbon.

Since each carbon atom is bonded to four other atoms, its bonding orbitals (sp^3 orbitals) are directed toward the corners of a tetrahedron.

As in the case of methane, the carbon-hydrogen bonds result from overlap of these sp^3 orbitals with the s orbitals of the hydrogens. The carbon-carbon bond arises from overlap

of two sp^3 orbitals. The carbon-hydrogen and carbon-carbon bonds have the same general electron distribution, being cylindrically symmetrical about a line joining the atomic nuclei because of this similarity in shape, the bonds are given the same name, a bonds (sigma bonds). methane, the carbon-hydrogen bonds result from overlap of these sp^3 orbitals with the s orbitals of the hydrogens. The carbon-carbon bond arises from overlap of two sp^3 orbitals.

IUPAC names of alkanes

PREPARATION OF ALKANES

1. Hydrogenation of alkenes.

2. Reduction of alkyl halides

(a) - Hydrolysis of Grignard reagent

(b) – Reduction by metal and acid.

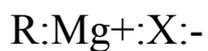
3. Coupling of alkyl halides with organometallic compounds.

Reduction of alkyl halide

either via the Grignard reagent or directly with metal and acid, involves simply the replacement of a halogen atom by a hydrogen atom; the carbon skeleton remains intact.

The Grignard reagent: an organometallic compound

The Grignard reagent has the general formula RMgX , and the general name alkylmagnesium halide. The carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium-halogen bond is essentially ionic.



since magnesium becomes bonded to the same carbon that previously held halogen, the alkyl group remains intact during the preparation of the reagent. Thus n-propyl chloride yields n-propylmagnesium chloride, and isopropyl chloride yields isopropylmagnesium chloride.

REACTIONS OF ALKANES

.1. Halogenation.

2. Combustion.

Halogenation

As we might expect, halogenation of the higher alkanes is essentially the same as the halogenation of methane. It can be complicated, however, by the formation

of mixtures of isomers. Under the influence of ultraviolet light, or at 250-400, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkanes (alkyl

bromides); an equivalent amount of hydrogen chloride or hydrogen bromide is formed at the same time. When diluted with an inert gas, and in an apparatus designed to carry away the heat produced, fluorine has recently been found to give

analogous results. As with methane, iodination does not take place at all.

Combustion

The reaction of alkanes with oxygen to form carbon dioxide, water, and most important of all heat* is the chief reaction occurring in the internal combustion engine; its tremendous practical importance is obvious.

The mechanism of this reaction is extremely complicated and is not yet fully understood.

Alkenes Structure and Preparation

Unsaturated hydrocarbons (C_nH_{2n})

In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the alkenes, which contain less hydrogen, carbon for carbon, than the alkanes, and which can be converted into alkanes by addition of hydrogen.

The alkenes were further described as being obtained from alkanes by loss of hydrogen in the cracking process . Since alkenes evidently contain less than the maximum quantity of hydrogen, they are referred to as unsaturated hydrocarbons. This unsaturation can be satisfied by reagents other than hydrogen and gives rise to the characteristic chemical .

properties of alkene

structure of ethylene. The carbon-carbon double bond

The simplest member of the alkene family is ethylene, C_2H_2 . In view of the ready conversion of ethylene into ethane, we can reasonably expect certain structural similarities between the two compounds. To start, then, we connect the carbon atoms by a covalent bond, and then attach two hydrogen atoms to each carbon atom. At this stage we find that each carbon atom possesses only six electrons in its valence shell, instead of the required eight, and that the entire molecule needs an additional pair, of electrons if it is to be neutral. We can solve both these problems by assuming that the carbon atoms can share two pairs of electrons. To describe this sharing of two pairs of electrons, we say that the carbon atoms are joined by a double bond. The carbon-carbon double bond is the distinguishing feature of the alkene structure

$H:C::C:H$ Atomic orbitals: hybrid Sp^2 orbitals. Axes

directed toward corners of equilateral triangle.

The molecule is not yet complete, however. In forming the sp^2 orbitals, each carbon atom has used only two of its three p orbitals. The remaining p orbital consists of two equal lobes, one lying above and the other lying below the plane of the three sp^2 orbitals. It is occupied by a single electron. If the p orbital of one carbon atom overlaps the p orbital of the other carbon atom, the electrons pair up and an additional bond is formed. Because it is formed by the overlap of p orbitals, and to distinguish it from the differently shaped σ bonds, this bond is called a π bond (pi bond). Because of less overlap, the π bond is weaker than the carbon-carbon σ bond.

Names of alkenes

The rules of the IUPAC system are:

1. Select as the parent structure the longest continuous chain that contains the carbon-carbon double bond. The parent structure is known as ethane, propene, butene, pentene, each name is derived by changing the ending -ane of the corresponding alkane name to -ene:

$\text{H}_2\text{C}=\text{CH}_2$, $\text{CH}_3\text{-CH}=\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CHCH}_3$

Ethene

Propene

1-Butene

2-Butene

Cis or tras

2---Indicate by a number the position of the double bond in the parent chain. Although the double bond involves two carbon atoms, designate its position by the number of the first doubly-bonded carbon encountered when numbering from the end of the chain nearest the double bond; thus 1-butene and 2-butene.

3. Indicate by numbers the positions of the alkyl groups attached to the parent chain.

Industrial source

Alkenes are obtained in industrial quantities chiefly by the cracking of petroleum. The smaller alkenes can be obtained in pure form by fractional distillation and are thus available for conversion into a large number of important aliphatic compounds. Higher alkenes, which cannot be separated from the complicated cracking mixture, remain as valuable components of gasoline.

1-Alkenes of even carbon number, consumed in large quantities in the manufacture of detergents, are available through controlled ionic polymerization of ethylene by the Ziegler-Natta method .

Preparation of alkenes

1. Dehydrohalogenation of alkyl halides.

Alkyl halides are converted into alkenes by dehydrohalogenation: elimination of the elements of hydrogen and halide.

Dehydrohalogenation involves removal of the halogen atom together

with a hydrogen atom from a carbon adjacent to the one bearing the halogen. It is not surprising that the reagent required for the elimination of what amounts to a molecule of acid is a strong base. The alkene is prepared by simply heating together the alkyl halide and a solution of potassium hydroxide in alcohol. For example

Carbonium ion

Before we can discuss the preparation of alkenes by dehydration of alcohols, we must first learn something about another kind of reactive particle: the carbonium ion, a group of atoms that contains a carbon atom bearing only six electrons. Carbonium ions are classified as primary, secondary, or tertiary after the carbon bearing the positive charge. They are named by use of the word cation. For example:

2- Dehydration of alcohols.

Alcohols are compounds of the general formula, ROH, where(R) is any alkyl group: the hydroxyl group, OH, is characteristic of alcohols, just as the carboncarbon double bond is characteristic of alkenes. An alcohol is named simply by naming the alkyl group that holds the hydroxyl group and following this by the word alcohol. It is classified as primary (1), secondary (2), or tertiary (3), depending upon the nature of the carbon atom holding the hydroxyl group .

For example:

3-Dehalogenation of vicinal dihalides.

4-Reduction of alkynes.

Alkenes Reactions

Reaction of the

Carbon Carbon Double Bond

Alkene chemistry is the chemistry of the carbon-carbon double bond. What kind of reaction may we expect of the double bond?

The double bond consists of a strong σ bond and a weak π bond; we might expect, therefore, reaction would involve the breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort,

where the π bond is broken and two strong σ bonds are formed in its place. A reaction in which two molecules combine to yield a single molecule of product is called an addition reaction. The reagent is simply added to the organic molecule,

1- Addition of hydrogen. Catalytic hydrogenation.

2. Addition of halogens.

3. Addition of hydrogen halides.

4. Addition of sulfuric acid.

5. Addition of water. Hydration.

6. Halohydrin formation.

7. Dimerization.

ALKYNES

Acetylene molecule: to be a linear molecule. The CC distance is 1.21 Å, as compared with 1.34 Å in ethylene and 1.53 Å in ethane. As in the case of the double bond, the structure of the triple bond is verified although this time in a negative way by the evidence of isomer number. As we can readily see from models, the linearity of the bonding should not permit geometric isomerism no such isomers have ever been found. The CH distance in acetylene is 1.08 Å, even shorter than in ethylene (1.103 Å); because of their greater s character .

s. Nomenclature

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups.

For more complicated alkynes the IUPAC names are used. The rules are exactly the same as for the naming of alkenes, except that the ending (-yne) replaces (-ene). The parent structure is the longest continuous chain that contains the triple bond, and the positions both of substituents and of the triple bond are indicated by numbers. The triple bond is given the number of the first triply-bonded carbon encountered, starting from the end of the chain nearest the triple bond.

Industrial source of acetylene

The alkyne of chief industrial importance is the simplest member of the family, acetylene. It can be prepared by the action of water on calcium carbide, CaC_2 , which itself is prepared by the reaction between calcium oxide and coke at the very high temperatures of the electric furnace. The calcium oxide and coke are in turn obtained from limestone and coal, respectively. Acetylene is thus obtained by a few steps from three abundant, cheap raw materials: water, coal, limestone

PREPARATION OF ALKYNES

1. Dehydrohalogenation of alkyl dihalides.

2. Reaction of sodium acetylides with primary alkyl halides.

3- Dehalogenation of tetrahalides.

REACTIONS OF ALKYNES

Addition Reactions

1- Addition of hydrogen .

2- Addition of halogens.

3. Addition of hydrogen halides.

2. Addition of water. Hydration.

Reactions as Acids

3. Formation of heavy metal acetylides.

6. Formation of alkali metal acetylides.

DIENES

Structure and nomenclature of dienes

Dienes are simply alkenes that contain two carbon-carbon double bonds. They therefore have essentially the same properties as the alkenes we have already. Dienes are named by the IUPAC system in the same way as alkenes, except that the ending -diene is used, with two numbers to indicate the positions of the two double bonds. This system is easily extended to compounds containing any number of double bonds.

Dienes are divided into two important classes according to the arrangement of the double bonds, Double bonds that alternate with

single bonds are said to be conjugated; double bonds that are separated by more than one single bond are said to be isolated.

A third class of dienes, of increasing interest to organic chemists, contain cumulated double bonds; these compounds are known as allenes:

Preparation and properties of dienes

Dienes are usually prepared by adaptations of the methods used to make simple alkenes. For example, the most important diene, 1,3-butadiene (used to make synthetic rubber, has been made in this country by a cracking process, and in Germany by dehydration of an alcohol containing two OH groups:

The chemical properties of a diene depend upon the arrangement of its double bonds. Isolated double bonds exert little effect on each other, and hence each reacts as though it were the only double bond in the molecule. Except for the consumption of larger amounts of reagents, then, the chemical properties of the non-conjugated dienes are identical with those of the simple alkenes. Conjugated dienes differ from simple alkenes in three ways: (a) they are more stable, (b) they undergo 1,4-addition, and (c) toward free radical addition, they are more reactive.

