Organic Chemistry

an introduction

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❋ lecture notes on "Basics of Organic chemistry" by Dr.Anandhi Sridharan, Christ University, Bangalore (2009)

Introduction

Organic chemistry is the study of carbon compounds. These organic compounds constitute essential compounds of our blood, muscles and skin. They are found in fuels, polymers, dyes and medicines.

1. Hybridisation of carbon

Carbon has the electronic configuration $1s^2 2s^2 2p^2$ (atomic number 6), therefore, it is expected to be bivalent, but it exhibits tetravalency. This is because it is assumed that one electron from the 2s orbital is promoted to the vacant 'P_z' orbital. Thus, by mixing the orbitals, 4 new equivalent orbitals containing one electron each are formed. The process of mixing of atomic orbitals of the same atom having comparable energies to form new orbitals, hybrid orbitals, is called ***hybridization***. This concept was developed by L.Pauling. The number of hybrid orbitals obtained is equal to the number of atomic orbitals mixed. The hybrid orbitals are identical in size, shape, orientations and energies. Hybridised orbitals are very useful in the explanation of the shape of molecular orbitals for molecules. Hybrid orbitals form stronger bonds than pure atomic orbitals because of greater overlap of atomic orbitals.

Depending on the number and nature of orbitals involved, different types of hybridization are possible for carbon:

1. sp hybridization
2. sp^2 hybridisation
3. sp^3 hybridisation

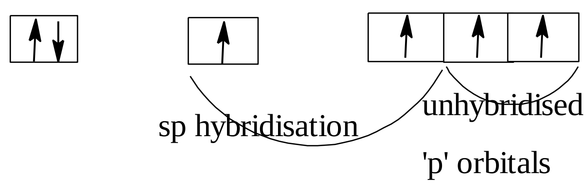
1. sp hybridization

Mixing of ‘2s’ and ‘2p’ orbitals of an atom to form two ‘sp’ hybrid orbitals is called sp hybridization. The two ‘sp’ hybrid orbitals are oriented at an angle of 180^0 with respect to each other. This hybridization is also known as diagonal or linear hybridization. E.g. acetylene

Formation of acetylene (C_2H_2) molecule

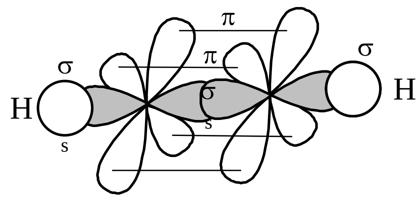
‘C’ in the ground state $1s^2$ $2s^2$ $2p^2$

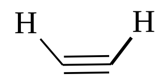
‘C’ in the excited state



One electron from the ‘2s’ orbital is promoted to the vacant ‘P_z’ orbital in the excited state of carbon. So, ‘2s’ orbital and one ‘2p’ orbital combine to give two ‘sp’ hybrid orbitals directed linearly at an angle of 180^0. After ‘sp’ hybridization, each carbon atom has two ‘sp’ hybrid orbitals and two unhybridised ‘p’ orbitals which lie mutually perpendicular to each other.

A ‘sp’ hybrid orbital of one carbon atom overlaps with a ‘sp’ hybrid orbital of the other carbon atom to form C-C σ bond. The remaining ‘sp’ hybrid orbital of each carbon atom overlaps with ‘s’ orbital of hydrogen atom to form C-H σ bond. After forming σ-bonds, each carbon atom is left with two unhybridised ‘p’ orbitals which are at right angles to each other. The unhybridised ‘p’ orbitals overlap laterally (sideways) to form two π-bonds.





Due to 'sp' hybridization, acetylene has linear structure.

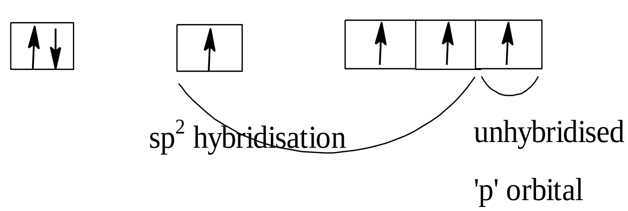
2. Sp^2 hybridization

Mixing of '2s' and two '2p' orbitals of an atom to form three 'sp^2' hybrid orbitals is called sp^2 hybridization. After sp^2 hybridization , each carbon atom has three sp^2 hybrid orbitals oriented at an angle of 120^0 with respect to each other and point towards the three corners of an equilateral triangle. In the same plane and one unhybridised 'P_z' orbital which is at right angles to the plane of the hybrid orbitals. This hybridization is also known as trigonal hybridization. E.g. ethylene

Formation of ethylene (C_2H_4) molecule

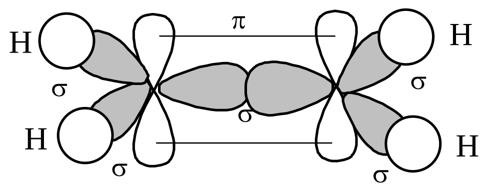
'C' in the ground state $1s^2$ $2s^2$ $2p^2$

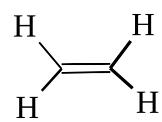
'C' in the excited state



One electron from the '2s' orbital is promoted to the vacant 'P_z' orbital in the excited state of carbon. So, one '2s' orbital and two '2p' orbitals combine to form three 'sp^2' hybrid orbitals with a bond angle of 120^0. After 'sp^2' hybridization, each carbon atom has three 'sp^2' hybrid orbitals and one unhybridised 'p' orbital.

A 'sp^2' hybrid orbital of one carbon atom overlaps with a 'sp^2' hybrid orbital of the other carbon atom to form C-C σ bond. The remaining two 'sp^2' hybrid orbital of each carbon atom overlaps with 's' orbitals of two hydrogen atoms to form two C-H σ bonds. After forming σ-bonds, each carbon atom is left with one unhybridised 'p' orbital. The unhybridised 'p' orbitals overlap laterally (sideways) to form a π-bond.





Due to sp^2 hybridisation, ethylene has planar structure. π electron density lies above and below the plane.

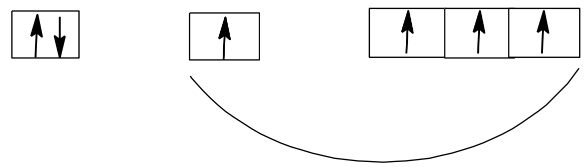
3. Sp^3 hybridization

Mixing of '2s' and three '2p' orbitals of an atom to form four 'sp^3' hybrid orbitals is called <u>sp^3 hybridization</u>. After sp^3 hybridization , each carbon atom has four sp^3 hybrid orbitals which are directed in space at an angle of $109^0 28'$ and point towards the four corners of a regular tetrahedron. E.g. methane

<u>Formation of methane (CH_4) molecule</u>

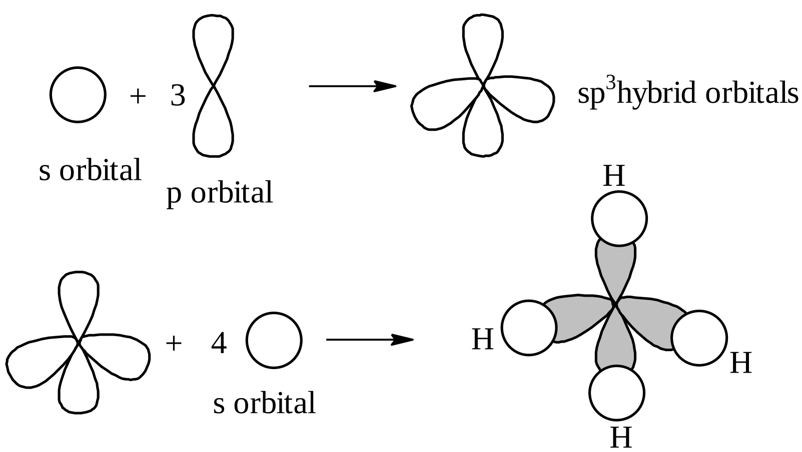
'C' in the ground state $1s^2$ $2s^2$ $2p^2$

'C' in the excited state



sp^3 hybridisation

One electron from the '2s' orbital is promoted to the vacant 'P_z' orbital in the excited state of carbon. So, one '2s' orbital and three '2p' orbitals combine to form four 'sp^3' hybrid orbitals oriented towards four corners of a regular tetrahedron. After 'sp^2' hybridization, each carbon atom has four 'sp^3' hybrid orbitals and each orbital has one electron. Each 'sp^3' hybrid orbital of one carbon atom overlaps with 's' orbitals of four hydrogen atoms to form four C-H σ bonds.



CH_4

Due to sp^3 hybridisation, methane has tetrahedral structure with a bond angle of $109^0 28'$.

<u>Comparison of sp, sp^2 and sp^3 hybrid orbitals of carbon</u>

The percent of 's' or 'p' orbital in a hybrid orbital is calculated by:

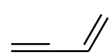
Number of 's' or 'p' orbitals mixed÷Total number of orbitals mixed

Therefore, ‘sp’ orbital will have 50%‘s’ and 50% ‘p’ character. sp^2 will have 33.33% of‘s’ and 66.67% of ‘p’ character. sp^3 will have 25% of‘s’ and 75% of ‘p’ character. Hybridisation influences the bond length and bond strength in organic compounds. ‘sp’ hybrid orbital forms shorter and stronger bonds than sp^2 or sp^3. This is because it contains more‘s’ character and‘s’ orbital is closer to the nucleus and hence form strong bonds. Based on the contribution of‘s’ or ‘p’ character, we can observe the following characteristics:

1. Size of a hybrid orbital increases with decrease of‘s’ character in it. Hence the relative sizes of hybrid orbitals are :
   sp^3 › sp^2 › sp
2. The electro negativity of an orbital increases with increase of‘s’ character in it. Therefore,
   sp^3 ‹ sp^2 ‹ sp

Multiple Choice Questions

1. The molecule which has the largest distance between 2 carbon atoms is
(a) Ethane (b) ethene (c) ethyne (d) benzene

2. The hybridization of carbon atoms in C-C bond in  is
(a) sp^3-sp^3 (b) sp^2-sp^3 (c) sp-sp^2 (d) sp^3-sp

3. The correct order for the size of hybrid orbital of carbon is
(a) sp›sp^2›sp^3 (b) sp‹sp^2‹sp^3 (c) sp›sp^2‹sp^3 (d) sp‹sp^2›sp^3

4. The Cl-C-Cl angle in 1,1,2,2-tetrachloroethene and tetra chloromethane will be
(a) 120^0 and 109.5^0 (b) 109.5^0 and 90^0 (c) 90^0 and 109.5^0 (d) 109.5^0 and 120^0

5. Which of the following statements is not correct?
(a) sp hybrid orbital is more electronegative than sp^2 hybrid orbital.

(b) The size of sp^3 hybrid orbital of carbon is smaller than that of sp hybrid orbital.

(c) The C-H bond length is maximum in methane compared to ethane and acetylene.

(d) The resonating structures do not differ in the number of unpaired electrons.

Answers

1. (a) 7. (c) 8. (b) 9. (a) 10. (b)

Solutions

6. The bond length of C-C decreases with increase in the number of bonds between 2 carbon atoms. Accordingly, the bonds in ethane are all single bonds and hence largest distance compared to ethane and ethyne and benzene, which have multiple bonds.

2. There is a triple bond and a double bond in the given compound. Therefore, sp and sp^2 hybridisation of carbon atoms are involved in this case.

3. Size of a hybrid orbital increases with decrease of‘s’ character in it. Hence the relative sizes of hybrid orbitals are :

   $sp‹sp^2‹sp^3$

4. In tetrachloroethene, each of the carbon atoms is sp^2 hybridised. Therefore, the bond angle is 120^0. In tetra chloromethane, each carbon atom is sp^3 hybridised and hence the bond angle is 109.5^0.

5. Normally, the size of a hybrid orbital increases with decrease of‘s’ character in it.

2. *σ and π bonds*

A covalent bond between 2 atoms is formed by overlapping of 2 atomic orbitals – one electron from each atom. Depending on the overlap of atomic orbitals, a covalent bond may be either a σ-bond or a π-bond. When the two half-filled atomic orbitals overlap end-to-end or head-to-head along their axes, it is called a ***σ-bond***. All σ-bonds have axial symmetry. Since the overlap of 2 orbitals along their axes is maximum, σ-bond is a strong bond. When the two half-filled atomic orbitals overlap side-to-side or laterally along a line perpendicular to the molecular axis, it is called a ***π-bond***. π-bond is weaker than the σ-bond because the degree of overlapping is less.

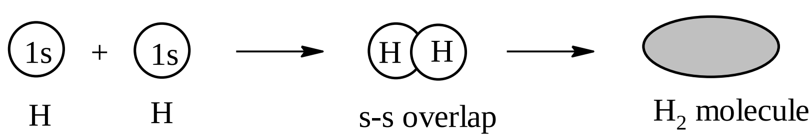
σ bond

If z-axis is assumed to be the molecular axis, σ bond is given by s-s, s-p and p-p overlaps. These σ-bonds are called s-s, s-p and p-p σ-bonds respectively.

(i) s-s overlap

E.g. formation of H_2 molecule

Hydrogen has only one 1s orbital and this can form only one covalent bond. The 1s orbitals of 2 hydrogen atoms overlap along their axes to form H_2 molecule.



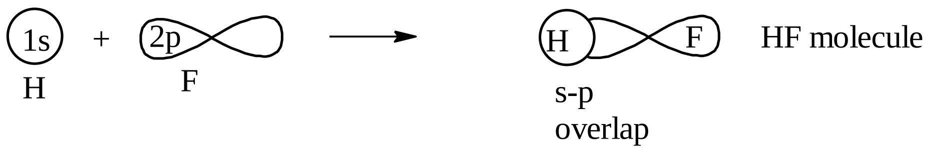
(ii) s-p overlap

E.g. formation of HF molecule

Electronic configuration of H: $1s^1$

Electronic configuration of F: $1s^1 2s^2 2p^5$

1s orbital of hydrogen overlaps with the 2p orbital of fluorine to form HF molecule.

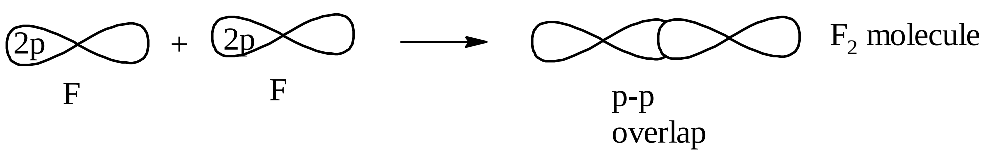


(iii) p-p overlap

E.g. formation of F_2 molecule

Electronic configuration of F: $1s^1 2s^2 2p^5$

2p orbital of one fluorine atom overlaps with the 2p orbital of the other fluorine atom to form F_2 molecule.



π bond

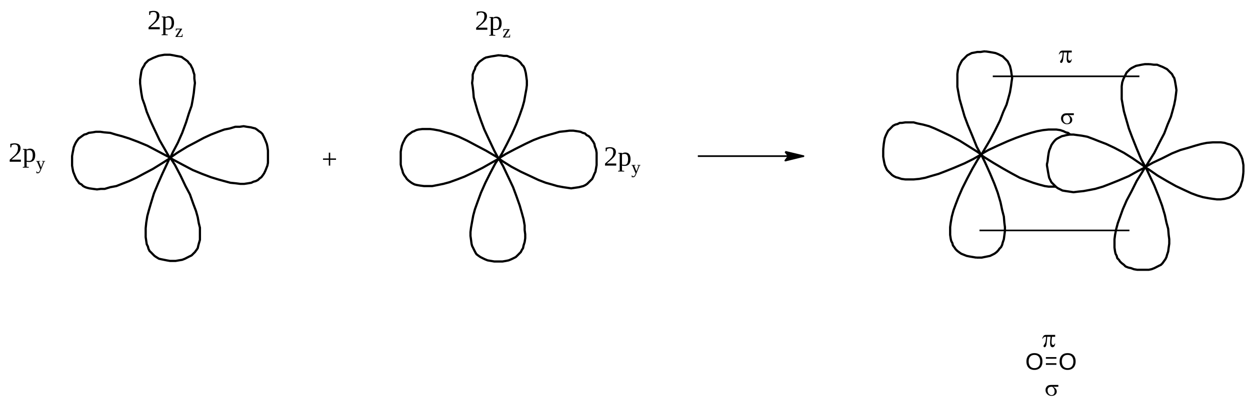
If z-axis is assumed to be the molecular axis, π-bond is given by p_x-p_x and p_y-p_y overlaps. They give π-bonds.

Examples:

(i) Formation of O_2 molecule

Electronic configuration of O: $1s^1 2s^2 2p^4$

$2p_y$ orbital of one oxygen atom will overlap with $2p_y$ orbital of the other oxygen atom to give a p_y- p_y σ-bond. The two $2p_z$ orbitals of both the oxygen atoms will overlap along a line perpendicular to the y-axis to give a p_z - p_z π-bond.

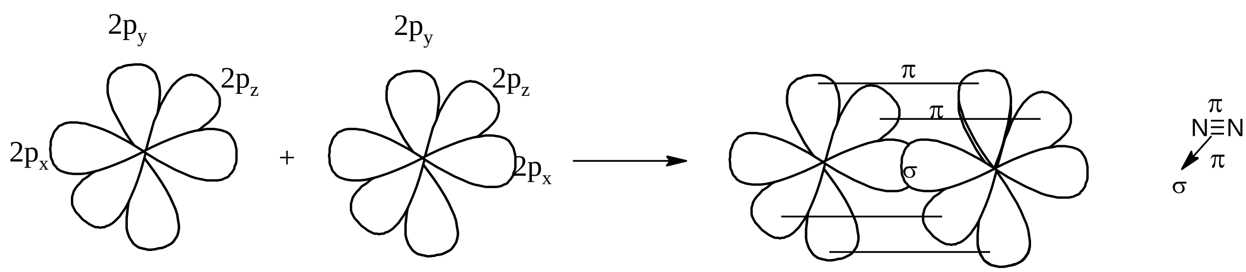


Therefore, oxygen has one σ-bond and one π-bond.

(ii) <u>Formation of N_2 molecule</u>

Electronic configuration of N: $1s^1 2s^2 2p^3$

$2p_x$ orbital of one nitrogen atom will overlap with $2p_x$ orbital of the other nitrogen atom to give a p_x- p_x σ-bond. The two $2p_z$ orbitals of both the oxygen atoms will overlap along a line perpendicular to the x-axis to give a p_z - p_z π-bond. The two $2p_y$ orbitals of both the oxygen atoms will overlap along a line perpendicular to the x-axis to give a p_y - p_y π-bond.



Therefore, nitrogen has one σ-bond and two π-bonds.

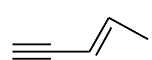
Differences between σ and π-bonds:

σ-bond	**π-bond**
σ-bond is formed by the axial overlap of s-s or s-p or p-p orbitals of 2 atoms.	Π-bond is formed by the lateral overlap of p-p orbitals.
σ-bond is stronger due to greater overlapping of atomic orbitals.	π-bond is weaker due to relatively less overlapping of atomic orbitals.
Only one σ-bond between 2 atoms.	One or two π-bonds between 2 atoms.
σ-bond can be rotated along the bond axis.	π-bond can't be rotated relative to one another along the bond axis.
σ-bond determines the direction of the bond and the extent of the internuclear distance.	π-bond has no primary effect on the direction of the bond, but shortens the internuclear distance.

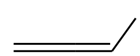
Multiple Choice Questions

6. The number of sigma and pi-bonds in 1-butene-3-yne are

(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi (c) 8 sigma and 2 pi (d) 6 sigma and 4 pi

7. How many sigma and pi bonds are present in 

(a) 10 sigma and 3 pi (b) 9 sigma and 4 pi (c) 10 sigma and 2 pi (d) 9 sigma and 3 pi

8. How many sigma and pi bonds are present in 

(a) 10 sigma and 3 pi (b) 9 sigma and 2 pi (c) 10 sigma and 2 pi (d) 9 sigma and 3 pi

Answers

6. (b) 12. (a) 13. (b)

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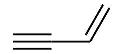
Solutions

11. The structure of compound, 1-butene-3-yne is  . From the structure, it is seen that there are 7 sigma bonds which includes four C-H and three C-C sigma bonds. There are 3 pi bonds which include one pi bond from the double bond and two pi bonds from a triple bond.
12. There are 10 sigma bonds (four C-C and six C-H bonds). There are 3 pi bonds (one pi bond from the double bond and two pi bonds from a triple bond).
13. There are 9 sigma bonds (three C-C and six C-H bonds). There are two pi bonds due to 2 double bonds.

3. *Determination of empirical and molecular formula of simple compounds (combustion method)*

Combustion analysis is used to determine the elemental composition of a given (pure) organic compound. Once we know the number of moles of each combustion product, the empirical formula of the given organic compound can be determined. ***Empirical formula*** is the smallest ratio of integers which yields the correct ratio of elements present in a compound. ***Molecular formula*** shows the exact number of atoms present in a molecule of the compound.

The empirical formula mass of a compound refers to the sum of the atomic masses of various atoms present in the empirical formula. From the empirical formula, the molecular formula can be calculated if you are given a molecular mass. Dividing the molecular mass by empirical formula mass, we get an integer called ‘n’. Once the value of ‘n’ is known, multiply the empirical formula by this number ‘n’ to get the molecular formula.

$$\text{Molecular mass} \div \text{Empirical formula mass} = n$$

$$\text{Molecular formula} = \text{Empirical formula} \times n$$

Therefore, molecular mass of a compound is a multiple of the empirical formula mass, i.e. molecular mass, M = n×empirical formula mass where 'n' is an integer (1, 2, 3, etc).

Examples of empirical and molecular formula

Example 1:

Suppose if 'C' and 'H' are present in a compound in a ratio of 1: 2, the empirical formula is CH_2. Therefore, empirical formula mass is 12.0+ (2×1) = 14g/mol
Given that the molecular mass of the compound is 28g/mol, the molecular formula of the compound can be calculated.

Molecular mass÷Empirical formula mass = n = 2

We know that molecular formula = n×empirical formula = $2 \times CH_2 = C_2H_4$

Example 2:

Calculation of the empirical formula from percentage composition.
An organic compound contains 84% carbon and 16% hydrogen (C = 12.0, H = 1.00) after combustion analysis. Determine the molecular formula of the organic compound.

Solution: There are many steps to arrive at the molecular formula of a given organic compound:
Step 1: The first step is to convert mass percent to grams. For this, we have to assume that the percentage composition of a given organic compound to be 100g, i.e. the total mass of a given compound is 100g. Accordingly, in this case, 84% of carbon will be 84g of carbon and 16% of hydrogen will be 16g of hydrogen.

100g (0.84) = 84g of carbon and
100g (0.16) = 16g of hydrogen

We have to compare these elements to each other stoichiometrically, for that; they should be expressed in terms of moles.

Step 2: Amounts of each element can be expressed in terms of moles of each element. This can be done by converting the mass of each element to moles of each element, which in turn can be done by dividing the mass of each element by its atomic weight. This will give an idea about the relative number of atoms in the compound. Therefore,

Moles of carbon = 84g÷12g = 7

Moles of hydrogen = 16g÷1.0g = 16

The atom ratio of C: H is 7:16.

Step 3: Once the number of moles of each element is known, the empirical formula can be determined. This can be achieved by dividing the mole value obtained above by the smallest value. Here the smallest mole quantity is carbon. Therefore,

7 mole C / 7 mole = 1 C

16 mole H / 7 mole = 2.286 H

The ratio of C: H is 1:2.286. The integer for carbon can't be 1 because this integer does not lead to an integer value for hydrogen.

Step 4: Since the above ratio is not a whole number, multiply each ratio by the smallest suitable integer so that a whole number ratio is obtained.

2.000: 4.572

3.000: 6.858

4.000: 9.144

5.000: 11.43

6.000: 13.716

7.000: 16.002 (now round it to the nearest whole number)

This is the actual mole ratio of the elements and is represented by the subscripts in the empirical formula. Thus the empirical formula is C_7H_{16}. Since it can't be any simpler, and in this case, the given organic compound has the molecular formula, **C_7H_{16}**, same as the empirical formula.

Please note that in most of the cases, after determining the empirical formula, one has to calculate the mass of the empirical formula. Molecular formula can be determined if you are given a molecular mass. The molecular mass is compared to the empirical formula mass to get an integer called 'n'. Once the value of 'n' is known, multiply the empirical formula by 'n' to get the molecular formula.

Example 3:

An organic compound contains 20.0% C, 6.66% H, 47.38% N and the rest was oxygen. Its molar mass is 60g/mol. Calculate the empirical and the molecular formula of the compound.

Solution:

Step 1: The first step is to convert mass percent to grams. The total mass of a given compound is 100g. In that, 20g of carbon, 6.66g of hydrogen, 47.33g of nitrogen and 26.01g of oxygen are present.

Step 2: Amounts of each element can be expressed in terms of moles of each element. Therefore,

Moles of carbon = 20g÷12g = 1.67
Moles of hydrogen = 6.66g÷1.0g = 6.66
Moles of nitrogen = 47.33g÷14g = 3.38
Moles of oxygen = 26.01g÷16g = 1.63

Step 3: Atom ratio of various elements in the given organic compound can be obtained by dividing the mole value of the respective element by the smallest mole value of the element. Therefore, the atom ratio of C: H: N: O is 1:4:2:1. Based on the atom ratio, the empirical formula is CH_4N_2O.

Step 4: After determining the empirical formula, the empirical formula mass is calculated by adding the atomic masses of various atoms present in the empirical formula. For CH_4N_2O, the empirical formula mass is 12.0×1+1.008×4+14×2+16×1 = 60g/mol

Step 5: Molecular formula can be determined using a given molecular mass. The molecular mass is compared to the empirical formula mass to get an integer called 'n'.

$$\text{Molecular mass} \div \text{Empirical formula mass} = n = 1$$

Step 6: Once the value of 'n' is known, multiply the empirical formula by 'n' to get the molecular formula. Therefore,

Empirical formula×n = $CH_4N_2O \times 1 = CH_4N_2O$ = molecular formula

Hence the molecular formula of the compound is CH_4N_2O.

Multiple Choice Questions

7. An organic compound contains 40% C, 6.72% H, and 53.28% O. Its molar mass is 180.18g/mol. The molecular formula of the compound is
   (a) $C_6H_{12}O_6$ (b) $C_5H_{10}O_6$ (c) $C_7H_{14}O_7$ (d) $C_6H_{11}O_6$

8. A certain organic compound contains 47.5% C, 2.54% H and 50% Cl by mass. The empirical formula is
   (a) $C_{13}H_8Cl_5$ (b) $C_{14}H_9Cl_5$ (c) $C_{12}H_{10}Cl_5$ (d) $C_{15}H_{12}Cl_5$

9. The molecular formula for a compound containing 85.6% C and 14.4% H by mass is
   (a) CH (b) CH_2 (c) C_2H_3 (d) CH_3

10. What is the percentage of C, H and O in ethanol?
   (a) 48,12, 35 (b) 49.2,13.4,37.6 (c) 53,14.1,38.5 (d) 52.14,13.13, 34.73

11. The combustion of 4.25mg of an organic compound produces 8.45mg of CO2 and 3.46mg of water. The mass percentages of C and H in the compound are
   (a) 54.4, 9.1 (b) 9.1, 54.4 (c) 27.2, 18.2 (d) 18.2, 27.2

Answers

1. (a) 2. (b) 3. (b) 4. (d) 5. (a)

Solutions

9. A 100g compound contains 40g of carbon, 6.72g of hydrogen and 53.28g of oxygen. Based on these masses, we can calculate the number of moles of each element. Therefore,

$$\text{Moles of carbon} = 40g \div 12g = 3.33$$
$$\text{Moles of hydrogen} = 6.72g \div 1.0g = 6.72$$
$$\text{Moles of oxygen} = 53.28g \div 16g = 3.33$$

   Based on the number of moles of each element, the atom ratio of various elements in the given organic compound can be calculated. Therefore, the atom ratio of C: H: O is 1:2:1. Based on the atom ratio, the empirical formula is CH_2O.

   Now, we can calculate the empirical formula mass and it is found to be:
   $12\times1+1\times2+6\times1 = 30g/mol$

The next step is to find the number of empirical formula units in the molecular formula.

Molecular mass÷Empirical formula mass = n = 180.18÷30 = 6

The molecular formula is given by:

Empirical formula×n = CH_2O×6 = $C_6H_{12}O_6$ = molecular formula

Hence the molecular formula of the compound is $C_6H_{12}O_6$.

10. A 100g compound contains 47.5g of carbon, 2.54g of hydrogen and 50g of chlorine. Based on these masses, we can calculate the number of moles of each element. Therefore,

Moles of carbon = 47.5g÷12g = 3.96

Moles of hydrogen = 2.54g÷1.0g = 2.54

Moles of chlorine = 50g÷35.5g = 1.41

The ratio will be 2.8:1.8:1. Since all the values are not whole numbers, multiplying each ratio by the smallest suitable integer so that a whole number ratio is obtained. Accordingly, we get the atom ratio as 14:9:5.

Based on the atom ratio, the empirical formula is $C_{14}H_9Cl_5$.

11. A 100g compound contains 85.6g of carbon and 14.4g of hydrogen. Based on these masses, we can calculate the number of moles of each element. Therefore,

Moles of carbon = 85.6g÷12g = 7.13

Moles of hydrogen = 14.4g÷1.0g = 14.4

Based on the number of moles of each element, the atom ratio of various elements in the given organic compound can be calculated. Therefore, the atom ratio of C: H is 1:2. Based on the atom ratio, the empirical formula is CH_2.

12. Molecular formula of ethanol is C_2H_5OH.
    Therefore, molecular mass of ethanol is 2×12.01+6×1.008+16×1 = 46.068g

    Mass percent of carbon = 24.02g÷46.068×l00 = 52.14%

    Mass percent of hydrogen = 6.048g÷46.068×l00 = 13.13%

    Mass percent of oxygen = 16g÷46.068×l00 = 34.73%

13. Mass percent of carbon can be calculated from the amount of carbon dioxide formed from an organic compound. Therefore,

    Mass percent of carbon = (12÷44) × (8.45÷4.24) ×100 = 54.4%

    Mass percent of hydrogen can be calculated from the amount of water formed from an organic compound. Therefore,

    Mass percent of hydrogen = (2÷18) × (3.46÷4.24) ×100 = 9.1%