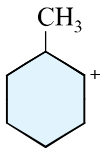
23. Which of the following carbocations can undergo rearrangement via hydride shift?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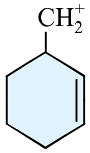
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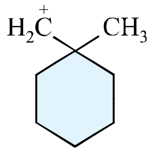
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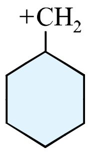

[4]

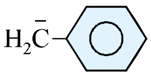
(A) 1 **(B)** 1 and 3 **(C)** 1, 4 **(D)** 1, 2, 4

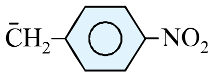
24. Which of the following species is most stable?

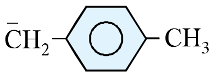
(A) $p-O_2NC_6H_4-\overset{\oplus}{C}H_2$ **(B)** $C_6H_5\overset{\oplus}{C}H_2$

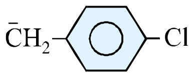
(C) $p-\ddot{\underset{\cdot\cdot}{Cl}}-C_6H_4-\overset{\oplus}{C}H_2$ **(D)** $p-H_3CO-C_6H_4-\overset{\oplus}{C}H_2$

25. Which one of the following is most stable ?


(A)


(B)


(C)


(D)

QUALITATIVE & QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS Section - 7

Qualitative Analysis :

Detection of functional groups is an important step in the analysis of organic compounds. It entirely depends on the correct determination of the constituent elements.

Elemental Detection :

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

Detection of Carbon and Hydrogen :

Carbon and Hydrogen are detected by heating the compound with copper (II) oxide. Carbon present in the compound reacts with copper (II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$\underset{\text{White}}{5H_2O + CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$$

Detection of Other Elements :

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place :

$$\mathrm{Na + C + N \xrightarrow{\Delta} NaCN}$$

$$\mathrm{2Na + S \xrightarrow{\Delta} Na_2S}$$

$$\mathrm{Na + X \xrightarrow{\Delta} Na\,X} \qquad (\mathrm{X = Cl, Br\ or\ I})$$

C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused masses by boiling it with distilled water. This extract is known as sodium fusion extract.

(A) Test for Nitrogen :

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue color confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

$$\mathrm{6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}}$$

$$\mathrm{3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}}$$

(B) Test for Sulphur :

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$\mathrm{S^{2-} + Pb^{2+} \longrightarrow \underset{(Black)}{PbS}}$$

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.

$$\mathrm{S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{Violet}{[Fe(CN)_5NOS]^{4-}}}$$

In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

$$\mathrm{Na + C + N + S \longrightarrow NaSCN}$$

$$\mathrm{Fe^{3+} + SCN^- \longrightarrow \underset{Blood\ Red}{[Fe(SCN)]^{2+}}}$$

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

$$\mathrm{NaSCN + 2Na \longrightarrow NaCN + Na_2S}$$

(C) Test for Halogens :

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$

X represents a halogen – Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

(D) Test for Phosphorus :

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow \underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Quantitative Elemental Analysis :

After determining the constituent elements of an organic compound, the next step is to determine their amounts by quantitative methods. The methods usually involve combustion, oxidation etc. of an organic compound so that they may change into such inorganic compounds as can be estimated either by volumetric or gravimetric method.

Estimation of Carbon and Hydrogen :

Liebig's Combustion Method : A weighed amount of the compound is heated in a current of dry air free from carbon dioxide or pure oxygen till the carbon of the compound changes to CO_2 and hydrogen into water. Carbon dioxide and water thus formed are trapped in a suitable apparatus and weighed.

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

The percentage composition is then calculated.

Calculation :

Let the weight of the sample = W g

Let the weight of water formed = x g (Increase in weight of $CaCl_2$ tube)

and let the weight of CO_2 formed = y g (Increase in weight of potash bulb)

Since 44 g of CO_2 are formed from 12 g of carbon,

$\therefore$ y g of CO_2 are formed from $\frac{12}{44} \times$ y g of carbon

Since 18 g of water are formed from 2 g of hydrogen,

∴ x g of water are formed from $\frac{2}{18} \times x$ g of hydrogen $= \frac{1}{9}x$ g of hydrogen

Now, W g of the substance contains $\frac{12}{44} \times$ y g of carbon

∴ 100 g of the substance contains $\frac{12 \times 100y}{44 \times W}$ g carbon

Again W g of the substance contain $\frac{x}{9}$ g of hydrogen

∴ 100 g of the substance contain $\frac{100x}{9W}$ g of hydrogen

∴ Percentage of carbon $= \frac{12 \times 100y}{44 \times W}$

and Percentage of hydrogen $= \frac{100x}{9W}$

Estimation of Nitrogen :

(i) **Duma's Method :** In this method the organic compound is heated with copper oxide strongly. Carbon, hydrogen and sulphur are oxidized to CO_2, H_2O and SO_2 respectively, while nitrogen is set free. These gases are passed through a nitrometer containing 30% KOH solution. Carbon dioxide and sulphur dioxide are absorbed, steam condenses and nitrogen collects by the displacement of KOH solution. From the volume of the collected nitrogen, the percentage of nitrogen is calculated.

$$C_xH_yN_z + CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + Cu$$

Calculation :

Let the weight of the sample = W g

Volume of moist N_2 = V cc

Room temperature = t°C

Barometric pressure = P mm

Aqueous tension at t°C = f mm

We know, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Or $\frac{(P-f)\times V}{(273+t)} = \frac{760 \times V_2}{273}$ (V_2 = Volume of N_2 at NTP)

$$V_2 = \frac{(P-f)\times 273 \times V}{760 \times (273+t)} \text{ cc}$$

Volume of N_2 at NTP in cc $= \frac{(P-f)\times 273 \times V}{760 \times (273+t)}$

Now, 22400 cc of N_2 at NTP weigh 28 g.

$$\therefore \quad \frac{(P-f)\times 273\times V}{760\times(273+t)} \text{ at NTP weigh } \left[\frac{28(P-f)\times 273\times V}{760\times 22400(273+t)}\right] g$$

$$\text{W g of the substance contain } \frac{28(P-f)\times 273\times V}{760\times 22400(273+t)} \text{ g } N_2$$

$$\therefore \quad \text{100 g of the substance contains } \frac{28(P-f)\times 273\times V\times 100}{760\times 22400W(273+t)} \text{ g}$$

$$\text{Percentage of Nitrogen} = \frac{28}{22400}\times\frac{\text{Volume of } N_2 \text{ at NTP}}{\text{Weight of substance}}\times 100$$

(ii) **Kjeldahl's Method :** The principle of this method is that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen is converted into ammonium sulphate. The resulting solution on treatment with excess of sodium hydroxide solution gives off ammonia. Ammonia is then absorbed in excess of standard sulphuric acid. The amount of ammonia and hence the amount of nitrogen is determined by finding the amount of acid neutralized by back titration of the residual acid with a standard alkali solution. From this the percentage of nitrogen is calculated. This method is not good for those nitrogen compounds which produce nitrogen gas N_2 on heating such as compound containing N in ring, nitro compounds, azo compounds etc.

Calculation :

Let the weight of the substance = W g and let V cc of N acid is required to neutralize the ammonia evolved.

$\therefore$ V cc of N acid = V cc of N NH_3

1000 cc of N NH_3 = 17 g of NH_3 = 14 g of nitrogen

$$\text{V cc of N } NH_3 = \frac{14}{1000}\times V\times N = 0.014\ NV \text{ g}$$

$$\therefore \quad \text{Percentage of nitrogen} = \text{Weight of nitrogen}\times\frac{100}{\text{Weight of substance}} = \frac{0.014\times N\times V\times 100}{W}$$

Estimation of Halogen :

(i) **Carius Method :** The compound containing halogen is heated with fuming nitric acid in a sealed tube (Carius tube) in presence of silver nitrate. Carbon and hydrogen present are oxidized to carbon dioxide and water. The halogens react with silver nitrate to give the precipitate of silver halide. The precipitate is collected, washed, dried and weighed.

Calculation :

Let the weight of the substance be W g.

Weight of the silver halide be y g.

$$\text{Weight of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Molecular weight of silver halide}}\times y \text{ g}$$

$$\therefore \quad \text{Percentage of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Molecular weight of silver halide}}\times y\times\frac{100}{W}$$

Estimation of Sulphur :

The compound is heated with fuming nitric acid. Sulphur present is oxidized to sulphuric acid. Barium chloride solution is added. The precipitate of barium sulphate is obtained. It is collected, washed, dried and weighed.

$$\%\text{ of Sulphur} = \frac{\text{Weight of } BaSO_4}{\text{Molecular weight of } BaSO_4} \times \frac{\text{Atomic weight of Sulphur}}{\text{Weight of Organic compound}} \times 100$$

Silver Salt method for determining molecular weight of Organic acids :

This method is based on the fact that organic acids form insoluble silver salts which on ignition leave a residue to metallic silver.

A small quantity of organic acid is treated with water or a suitable solvent and then a slight excess of ammonia solution added. The solution is boiled to expel excess of ammonia. Excess of silver nitrate solution is added to this solution when a white precipitate of insoluble silver salt is obtained. The precipitate is filtered and washed successively with water, alcohol and ether and then dried in an air oven.

A known weight of the silver salt is taken in a weighed crucible and ignited till decomposition is complete. The crucible is cooled and then weighed. Heating, cooling and weighing is continued till the final weight is constant.

Calculation :

Weight of crucible + lid = W g

Weight of crucible + lid + silver salt = W_1 g

Weight of crucible + lid + residual silver = W_2 g

Weight of silver salt = $(W_1 - W)$ g

And weight of silver = $(W_2 - W)$ g

$(W_2 - W)$ g of silver is obtained from $(W_1 - W)$ g of silver salt.

108 g of silver is obtained from $\frac{(W_1 - W) \times 108}{(W_2 - W)}$ g of silver salt.

$$\text{Equivalent weight of silver salt} = \frac{(W_1 - W) \times 108}{(W_2 - W)}$$

But equivalent weight of acid = Equivalent weight of Ag salt – 108 + 1 = Equivalent weight of Ag salt - 107

$$\therefore \quad \text{Molecular weight of the acid} = \left\{\frac{(W_1 - W) \times 108}{(W_2 - W)} - 107\right\} \times n \quad (\text{where } n = \text{basicity of the acid})$$

Platinichloride method for determining molecular weight of Organic Bases :

Organic bases (e.g. amines) form insoluble salts known as platinichlorides when treated with hydrochloroplatinic acid [H_2PtCl_6]. These salts are represented by the general formula $B_2H_2PtCl_6$, where B is one equivalent of the base. These salts on ignition leave a residue of metallic platinum.

The base is dissolved in HCl and a solution of platinic chloride $PtCl_4$ is added. The yellow crystalline salt that separates out is filtered, washed and dried. A known weight of the dried salt is ignited in a crucible.

Calculation :

Let X_1 g of the platinichloride leave on ignition X_2 g of platinum.

X_2 g of Pt is left by X_1 g of the salt on ignition.

195 g (At. weight of Pt) is left by $\left(\frac{X_1 \times 195}{X_2}\right)$ g of the salt on ignition.

Molecular weight of the salt $= \frac{X_1}{X_2} \times 195$

Molecular weight of $H_2PtCl_6 = 410$

Equivalent weight of base B $= \frac{M_{B_2H_2PtCl_6} - M_{H_2PtCl_6}}{2} = \frac{\left(\frac{X_1}{X_2} \times 195\right) - 410}{2}$

If the acidity of the base is n, then

Molecular weight of base $= \left[\left(\frac{X_1}{X_2} \times 195\right) - 410\right] \times \frac{n}{2}$

Illustration - 11 *0.25 g of an organic compound on combustion gave 0.495 g of CO_2 and 0.2025 g of H_2O. Calculate the percentage of carbon and hydrogen in the compound.*

SOLUTION :

Given weight of the substance = 0.25 g

Weight of CO_2 formed = 0.495 g

Weight of H_2O formed = 0.2025 g

44 g of CO_2 are formed from 12 g of carbon.

$\therefore$ 0.495 g are formed from $\frac{12}{44} \times 0.495$ of carbon

Now 0.25 g of the substance contains $\frac{12 \times 0.495}{44}$ g carbon.

$\therefore$ 100 g of the substance contains $\frac{12 \times 0.495 \times 100}{44 \times 0.25} = 54.55$ g

Since 18 g of H_2O are formed from 2 g of hydrogen.

$\therefore$ 0.2025 g H_2O are formed from $\frac{2}{18} \times 0.2025$ g hydrogen

Now, 0.25 g of the substance contains $\frac{2 \times 0.2025}{18}$ g hydrogen

$\therefore$ 100 g of the substance contains $\frac{2 \times 0.2025 \times 100}{0.25 \times 18} = 9.09$ g hydrogen

% of carbon = **54.55**

% of hydrogen = **9.09**

Illustration - 12 *0.159 g of an organic compound gave 14.01 cc of nitrogen at 19°C and 719.5 mm pressure by Duma's method. Calculate % of nitrogen in the organic compound. Given: Aqueous tension of water = 11.5 mm of Hg at 19°C.*

SOLUTION :

Aqueous tension at 19°C = 11.5 mm

We know,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

or $$\frac{(719.5-11.5)\times 14.01}{(273+19)} = \frac{760\times V_{N_2} \text{ at NTP}}{273}$$

$$V_{N_2} \text{ at NTP} = \frac{708\times 14.01\times 273}{760\times 292} \text{ cc}$$

Now, 22400 cc of N_2 at NTP weigh 28 g

∴ 1 cc of N_2 at NTP weigh $\frac{28}{22400}$ g

∴ $$\frac{708\times 14.01\times 273}{760\times 292}\text{cc} = \frac{28\times 708\times 14.01\times 273}{22400\times 760\times 292}\text{g}$$

0.159 g of the compound contains $\frac{28\times 708\times 14.01\times 273}{22400\times 760\times 292}$ g N_2

∴ 100 g of the compound contains $\frac{28\times 708\times 14.01\times 273\times 100}{22400\times 760\times 292\times 0.159} = 9.60\%$

Percentage of nitrogen = 9.60%

Illustration - 13 *0.69 g of an organic compound after heating with concentrated sulphuric acid was distilled with excess of NaOH. Ammonia liberated was passed into 100 cc of N HCl solution. The excess of the acid neutralized 80 cc of N NaOH. Calculate the percentage of nitrogen in the compound.*

SOLUTION :

80 cc of N NaOH = 80 cc of N HCl = Volume of residual acid

Volume of acid neutralized = (100-80) cc N HCl = 20 cc of N HCl = 20 cc of N NH_3

Now, 1000 cc N NH_3 = 14 g of nitrogen

20 cc N NH_3 = $\frac{14\times 20}{1000}$ g of nitrogen

0.69 g of the substance contains $\frac{14\times 20}{1000}$ g of nitrogen.

∴ 100 g of the substance contains $\frac{14\times 20\times 100}{0.69\times 1000} = 40$

∴ Percentage of nitrogen = **40%**

Illustration - 14 *0.26 g of an organic compound on heating with fuming nitric acid and silver nitrate give 0.31 g of silver bromide. Calculate the percentage of bromine in the compound.*

SOLUTION :

Now, $AgBr \longrightarrow Br$

or $(108+80)\,g \equiv 80\,g$

$\because$ 188 g of AgBr give 80 g of bromine.

$\therefore$ 0.31 g of AgBr give $\frac{80}{188} \times 0.31 = 0.1319\,g$ bromine

Now, 0.26 g of the substance give 0.1319 g bromine.

$\therefore$ 100 g of the substance gave

$$\frac{0.1319 \times 100}{0.26} = 50.7$$

$\therefore$ Percentage of bromine = **50.7**

Illustration - 15 *0.40 g of an organic compound gave 0.60 g of barium sulphate after Carius method. Find out the percentage of sulphur in the compound.*

SOLUTION :

Since, $BaSO_4 \equiv S$
233 g 32 g

233 g of $BaSO_4$ gives 32 g of sulphur.

0.60 g of $BaSO_4$ gives $\frac{32}{233} \times 0.60\,g$ of sulphur = 0.082 g sulphur

$\therefore$ Percentage of sulphur $= \frac{0.082}{40} \times 100 = 0.205\,\%$

Illustration - 16 *0.167 g of the silver salt of a monobasic organic acid left on ignition 0.108 g of silver. Calculate the molecular weight of the acid.*

SOLUTION :

Weight of Ag salt = 0.167 g and weight of Ag left = 0.108 g.

The weight of Ag salt that would leave 108 g of silver $= \frac{0.167}{0.108} \times 108 = 167\,g$

Equivalent weight of acid = 167 – 108 + 1 = 167 – 107 = 60

Molecular weight of the acid = 60 × 1 (basicity) = **60**

Illustration - 17 *Calculate the molecular weight of a monoacidic base, 0.298 g of whose platinichloride left 0.0975 g of platinum on ignition.*

SOLUTION :

Weight of the platinichloride = 0.298 g (X_1) and weight of platinum = 0.0975 g (X_2)

$$\text{Equivalent weight of the base} = \frac{\frac{0.298}{0.0975} \times 195 - 410}{2} = \frac{596 - 410}{2} = \frac{186}{2} = 93$$

Molecular weight of the base = 93 × 1 (acidity) = **93**

Illustration - 18 *A mono acid organic base on analysis gave the following results:* 0.10 *g of the base gave* 0.28 *g of* CO_2 *and* 0.075 *g of water and* 0.30 *g of the base gave* 31.32 *ml* N_2 *measured at* 15°C *and* 760 *mm,* 0.30 *g of the platinichloride left on ignition* 0.093 *g of platinum. What is the molecular formula of the base?*

SOLUTION :

The molecular formula is derived as follows

(a) Calculation of % of elements

$$\% \text{ of carbon} = \frac{12}{44} \times \frac{0.28}{0.10} \times 100 = 76.36\%$$

$$\% \text{ of hydrogen} = \frac{2}{18} \times \frac{0.075}{0.10} \times 100 = 8.33\%$$

$$\% \text{ of nitrogen} = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at NTP} \times 100}{\text{Weight of organic compound}}$$

$$\% \text{ of nitrogen} = \frac{28 \times 31.32 \times 100}{22400 \times 0.3} = 13.05\%$$

(b) Calculation of relative number of each atom:

$$C = \frac{76.36}{12} = 6.36\ ;\ H = \frac{8.33}{1} = 8.33 \text{ and } N = \frac{13.05}{14} = 0.90$$

(c) Calculation of simplest ratio:

$$C = \frac{6.35}{0.90} = 7\ ;\ H = \frac{8.33}{0.90} = 9 \text{ and } N = \frac{0.90}{0.90} = 1$$

(d) Determination of empirical formula:

It comes to be C_7H_9N, its empirical formula weight = 84 + 9 + 14 = 107

(e) Determination of molecular weight:

The molecular weight of the base is given by,

$$B = \frac{1}{2}\left[195 \times \frac{\text{Weight of hexachloroplatinate salt}}{\text{Weight of platinum}} - 410\right]$$

$$B = \frac{1}{2}\left[\frac{195 \times 0.3}{0.093} - 410\right] = \frac{1}{2}[629 - 410] = 109.5$$

$$B = 109.5$$

$$n = \frac{\text{Molecular weight}}{\text{Empirical weight}} = \frac{109.5}{107} \approx 1$$

Hence, molecular formula = empirical formula = $\mathbf{C_7H_9N}$

Illustration - 19 *A sample of a gaseous hydrocarbon occupying 1.12 litre at NTP was completely burnt in air and gave 2.2 g of CO_2 and 1.8 g of H_2O. Calculate the weight of compound taken and volume of O_2 at NTP required for its burning. Also calculate the molecular formula of the hydrocarbon.*

SOLUTION :

$$\text{Mole of compound} = \frac{\text{Volume evolved at NTP}}{\text{22400 ml or 22.4 litres}}$$

$$= \frac{1.12}{22.4} = 0.05 \text{ mol}$$

$$\text{Moles of } CO_2 \text{ produced} = \frac{2.2}{44} = 0.05 \text{ mol}$$

$$\text{Moles of } H_2O \text{ produced} = \frac{1.8}{18} = 0.10 \text{ mol}$$

Suppose the hydrocarbon is C_xH_y

$$\text{Then} \quad C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

$\therefore$ 1 mole of C_xH_y gives = 0.05 x mol of CO_2

$\therefore$ $0.05\,x = 0.05$

$$\therefore \quad x = \frac{0.05}{0.05} = 1$$

$$\text{Now, 1 mole of } C_xH_y \text{ gives} = \frac{y}{2} \text{ mol of } H_2O$$

$$\therefore \quad 0.05 \text{ mol of } C_xH_y \text{ will give} = 0.05\ \frac{y}{2} \text{ mol of } H_2O$$

$$0.05\ \frac{y}{2} = 0.10$$

$\therefore$ $y = 4$

Hence, the hydrocarbon is CH_4

$$\text{Weight of 1.12 litre } CH_4 \text{ at STP} = \frac{16 \times 1.12}{22.4} = 0.8\,g$$

Also, $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

1 mol of CH_4 requires 2×32 g oxygen

$\therefore$ 0.05 mol of CH_4 requires $2 \times 32 \times 0.05 = 3.2$ g CO_2

CH_4 requires O_2 = 3.2 g

Illustration - 20 *An organic compound, A containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. A on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67% silver. Deduce the structures of A and B.*

SOLUTION :

Percentage of oxygen $= 100 - (49.32 + 9.59 + 19.18) = 21.91$

Elements	Percentage composition	Atomic weight	Relative No. of atoms	Simplest ratio
C	49.32	12	$\frac{49.32}{12} = 4.11$	$\frac{4.11}{1.37} = 3$
H	9.59	1	$\frac{9.59}{1} = 9.59$	$\frac{9.59}{1.37} = 7$
N	19.18	14	$\frac{19.18}{14} = 1.37$	$\frac{1.37}{1.37} = 1$
O	21.91	16	$\frac{21.91}{16} = 1.37$	$\frac{1.37}{1.37} = 1$

Hence empirical formula of A $= C_3H_7NO$

Because A, gives NH_3 on boiling with NaOH, it can be an amide.

Now, silver salt of B, has 59.67% silver.

Hence equivalent weight of acid $= \left(\frac{100 \times 108}{59.67}\right) - 107 = 74$

Molecular weight of monobasic acid $= 74 \times 1 = 74$

Molecular formula of acid $= C_3H_6O_2$

$\therefore$ Structural formula of acid B is C_2H_5COOH.

Molecular formula of amide $= C_3H_7NO$.

Hence structural formula of amide (A) is $C_2H_5CONH_2$

IN-CHAPTER EXERCISE-E

Choose the correct alternative. Only One Choice is Correct. However, questions marked '*' may have More than One Correct option(s).

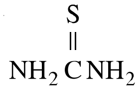
1. The percentage of sulphur in the organic compound, when 0.2595 g of a sulphur containing organic compound in a quantitative analysis by Carius method yieded 0.35 g of barium sulphate is :

(A) 14.52% **(B)** 16.52% **(C)** 18.52% **(D)** 19.52%

2. Which of the organic compounds will give red colour in Lassaigne test ?

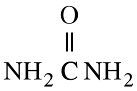
(A) NaCNS

(B)



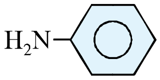
$NH_2C(=S)NH_2$

(C)



$NH_2C(=O)NH_2$

(D)



H_2N

3. If 0.228 g of silver salt of dibasic acid gave a residue of 0.162 g of silver on ignition, then molecular weight of the acid is:

(A) 70 **(B)** 80 **(C)** 90 **(D)** 100

***4.** For which compound Kjeldahl's method is not good for estimation of nitrogen.

(A) Pyridine **(B)** Nitrobenzene **(C)** Urea **(D)** Pyrrole

***5.** Which of the following compounds may give blood red colouration while performing Lassaigne's test for nitrogen?

(A) $(NH_2)_2CO$ **(B)** $(NH_2)_2C = S$

(C) p-$NH_2C_6H_4SO_3H$ **(D)** $C_6H_5SO_3H$

6. The compound that does not give a blue colour in Lassaigne's test is :

(A) Aniline **(B)** Glycine **(C)** Hydrazine **(D)** Urea

7. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because :

(A) Silver halides are soluble in HNO_3 **(B)** Na_2S and NaCN are decomposed by HNO_3

(C) Ag_2S is soluble in HNO_3 **(D)** AgCN is soluble in HNO_3

8. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is :

(A) Urea **(B)** Thiourea **(C)** Acetamide **(D)** Benzamide

9. In Lassaigne's test for nitrogen the blue colour is due to the formation of :

(A) Ferric-Ferro cyanide **(B)** $K_4[Fe(CN)_6]$

(C) $Na_4[Fe(CN)_6]$ **(D)** NaCN

10. 0.10 g of an organic compound containing phosphorus gave 0.222 g of $Mg_2P_2O_7$. Then the percentage of phosphorus in it is :

(A) 62 **(B)** 6.2 **(C)** 31 **(D)** 13

11. The silver salt of monobasic acid on ignition gave 60% of Ag. The molecular weight of the acid is :

(A) 37 **(B)** 33 **(C)** 73 **(D)** 77

ANSWERS TO IN-CHAPTER EXERCISES

A	**1.(i)** B	**(ii)** BD	**(iii)** BC	**(iv)** C	**(v)** D	**(vi)** AC	**(vii)** C
	(viii) D	**(ix)** A	**(x)** C				
B	**5.** B	**6.** D	**7.** B	**8.** C	**9.** C	**10.** C	**11.** A
	12. D						
C	**1.** AC	**2.** D	**3.** C	**4.** ABD	**5.** C	**6.** B	**7.** A
	8. B	**9.** D	**10.** AB	**11.** D	**12.** D	**13.** C	**14.** B
	15. B	**16.** B	**17.** BC				
D	**1.** B	**2.** B	**3.** ABD	**4.** C	**5.** A	**6.** B	**7.** B
	8. ABD	**9.** CD	**10.** A	**11.** D	**12.** A	**13.** ABC	**14.** ABCD
	15. B	**16.** B	**17.** A	**18.** A	**19.** B	**20.** ABCD	**21.** C
	22. A	**23.** D	**24.** D	**25.** B			
E	**1.** C	**2.** B	**3.** C	**4.** ABD	**5.** BC	**6.** C	**7.** B
	8. A	**9.** A	**10.** A	**11.** C			