



Structural Identification & Practical Organic Chemistry

Introduction

The main objective of an organic chemist is the determination of the structure of a new organic compound which has been obtained in pure state either from a natural source or synthesised in the laboratory.

In order to establish the correct structure of an organic compound, it is necessary to detect skeleton of compound, elements and functional groups present in the organic compounds.

Section (A) : Catalytic hydrogenation and Monohalogenation

A-1. Catalytic hydrogenation

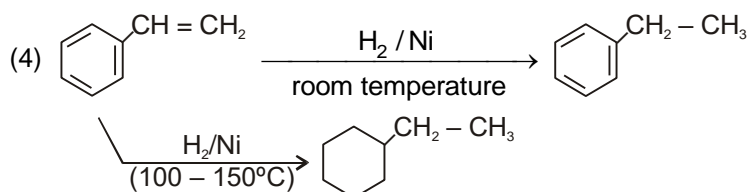
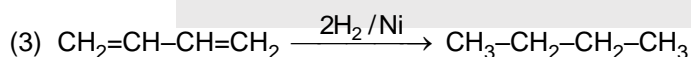
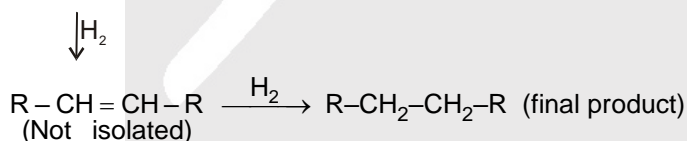
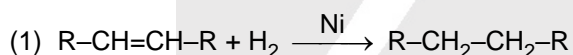
Alkenes, alkynes, polyalkenes or polyalkynes can be hydrogenated by using catalysts Ni/Pt/Pd at room temperature.

All carbon-carbon π bonds ($C=C$, $C\equiv C$) get hydrogenate in this reaction. The reaction can't stopped at any intermediate stage generally.

- Note :**
- (1) Aromatic π bonds are stable at room temperature but can be hydrogenated at high temperature.
 - (2) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated aliphatic compound is always a saturated compound.
 - (3) The number of moles of H_2 consumed by 1 mole of compound is equal to the number of π bonds.
 - (4) **During catalytic hydrogenation carbon skeleton does not change.**

Application : This reaction gives an information about how much unsaturation is present in the molecule.

General reaction :





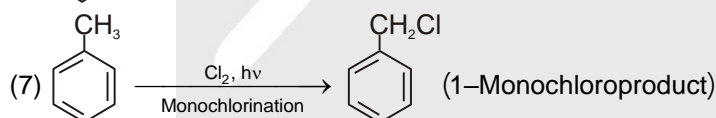
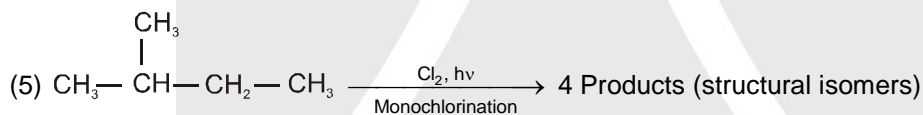
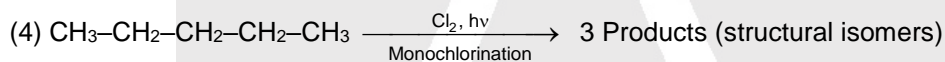
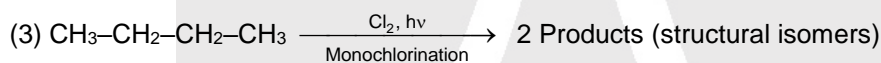
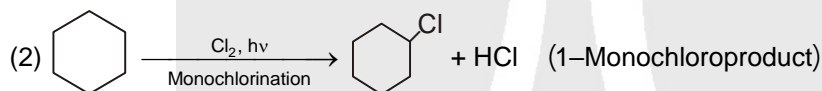
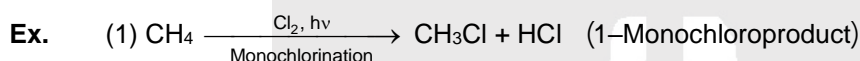
A-2. Monohalogenation

When an alkane or a cycloalkane is treated with halogen (Cl_2 , Br_2 , F_2 , I_2), a photochemical reaction takes place, in which a C–H bond is cleaved and a C–X bond is formed. In such reactions if one H-atom is substituted by one halogen atom, then this is known as monohalogenation reaction.

Applications : If a molecule has more than one type of H-atoms, then on monochlorination, it forms a mixture of monochloroisomers. **All these products (structures) are position isomers generally.**

Conclusion : It can be concluded that the total number of position isomers (structural) of monochloro compounds is equal to the number of different types of H-atoms present in the reactant. The different type of H-atoms are also known as non-identical hydrogen atoms (or non-equivalent hydrogen or chemically different hydrogen atoms).

- Note :** (1) In aromatic hydrocarbons, the hydrogen atoms of the saturated side-chain are chlorinated, but H-atoms of benzene ring are stable.
 (2) Generally chlorination and bromination reactions takes place.



- Note :** Only one monochloro product is formed in above reaction because aromatic H atoms are inert towards this reaction.

Section (B) : Ozonolysis reactions

Ozonolysis reaction is used to determine the position of $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$ in a molecule. In this reaction alkene, alkyne and polyalkene on ozonolysis undergo oxidative cleavage. It is of two types.

B-1 Reductive ozonolysis

Reagents : (1) O_3 (ozone) (2) Zn or $(\text{CH}_3)_2\text{S}$ and H_2O or CH_3COOH

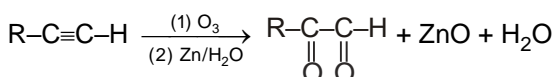
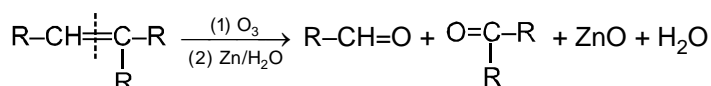
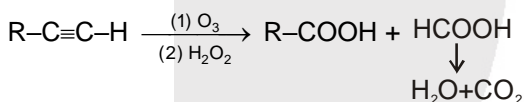
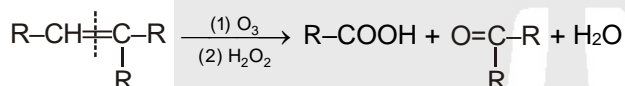
The products are carbonyl compounds (aldehydes or ketones) generally.


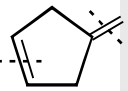
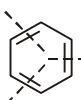
**B-2 Oxidative ozonolysis**

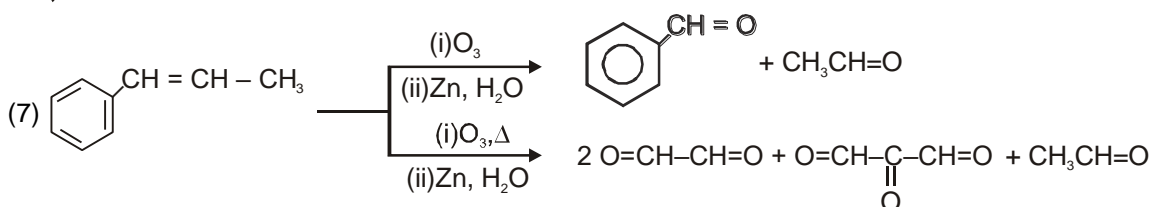
Reagents : (1) O₃ (ozone) (2) H₂O₂ or H₂O

The products are ketones and/or acids generally.

- Note :** (1) Ozonolysis does not interfere with other functional groups.
 (2) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

General reactions-**(a) Reductive ozonolysis****(b) Oxidative ozonolysis**

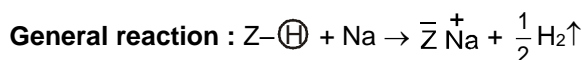
- Ex.** (1) $\text{CH}_2=\text{CH}_2 \xrightarrow[\text{(2) Zn/H}_2\text{O}]{\text{(1) O}_3} \text{CH}_2=\text{O} + \text{CH}_2=\text{O}$
- (2) $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 \xrightarrow[\text{(2) Zn/H}_2\text{O}]{\text{(1) O}_3} \text{CH}_3-\text{CH}_2-\text{CH}=\text{O} + \text{O}=\text{CH}_2$
- (3) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow[\text{(2) Zn/H}_2\text{O}]{\text{(1) O}_3} \text{CH}_2=\text{O} + \text{O}=\text{CH}-\text{CH}_2-\text{CH}=\text{O} + \text{O}=\text{CH}-\text{CH}_3$
- (4)  $\xrightarrow[\text{(2) Zn/H}_2\text{O}]{\text{(1) O}_3} 2\text{OHC}-\text{CH}_2-\text{CHO}$ (Propanedial)
- (5)  $\xrightarrow[\text{(2) Zn/H}_2\text{O}]{\text{(1) O}_3} \text{O}=\text{CH}-\text{CH}_2-\underset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\text{CH}=\text{O} + \text{O}=\text{CH}_2$
- (6)  $\xrightarrow[\text{(2) Zn/H}_2\text{O}]{\text{(1) O}_3} 3 \text{O}=\underset{\text{H}}{\underset{|}{\text{C}}}-\underset{\text{H}}{\underset{|}{\text{C}}}=\text{O}$ (Ethanedial) or (glyoxal)

**Section (C) : Tests for acidic hydrogen and unsaturation****C-1 Test for acidic hydrogen (Sodium metal test)**

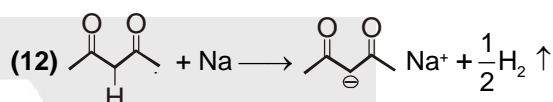
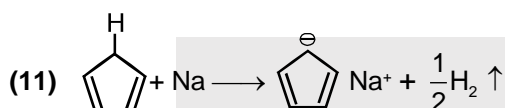
When any compound releases H₂ gas after reaction with sodium or potassium or alkali metals or sodamide then this reflects the presence of acidic hydrogen.



Active H : Those H atoms which are attached with more electronegative atoms like O,N,S,X, C_{sp} and active methylene.



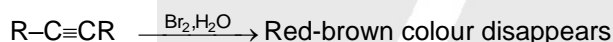
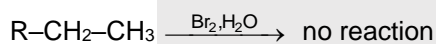
- Ex.**
- (1) $\text{R}-\text{NH}_2 \xrightarrow{\text{Na}} \text{R}-\text{NH}^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$ (2) $\text{R}-\text{SH} \xrightarrow{\text{Na}} \text{RS}^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$
- (3) $\text{R}-\text{COOH} \xrightarrow{\text{Na}} \text{R}-\text{COO}^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$ (4) $\text{PhOH} \xrightarrow{\text{Na}} \text{PhO}^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$
- (5) $\text{R}-\text{OH} + \text{Na} \rightarrow \text{R}-\text{O}^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$ (6) $\text{R}-\text{SO}_3\text{H} + \text{Na} \rightarrow \text{R}-\text{SO}_3^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$
- (7) $\text{R}-\text{C}\equiv\text{CH} + \text{Na} \rightarrow \text{R}-\text{C}\equiv\text{C}^-\text{Na}^+ + \frac{1}{2} \text{H}_2 \uparrow$ (8) $\text{R}-\text{CH}=\text{CH}_2 + \text{Na} \rightarrow \text{No reaction.}$
- (9) $\text{R}-\text{CH}_2-\text{O}-\text{CH}_3 + \text{Na} \rightarrow \text{No reaction.}$ (10) $\text{HCl} \xrightarrow{\text{Na}} \text{NaCl} + \frac{1}{2} \text{H}_2 \uparrow$



C-2 Test for unsaturation

(i) Bromine water test (Br₂ + H₂O, Red-brown solution)

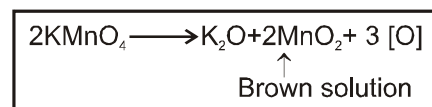
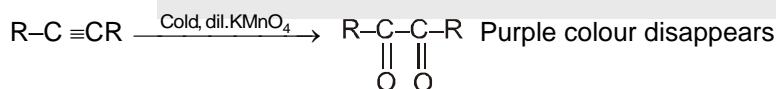
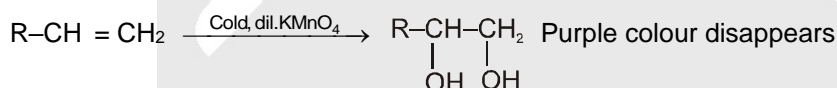
This is used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) hydrocarbons.



Note : Benzene does not give this test, whereas **phenol** and **aniline** give this test.

(ii) Baeyer's reagent (Cold dil. alkaline KMnO₄ Pink/purple solution)

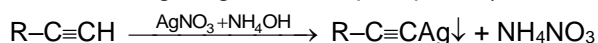
This is also used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) compounds.



C-3 Test for terminal alkynes

(i) Tollen's reagent [AgNO₃ + NH₄OH or {Ag(NH₃)₂}⁺ OH⁻]

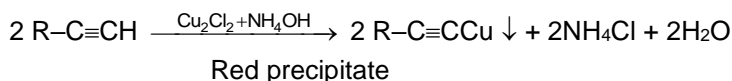
Tollen's Reagent gives white precipitate (Silver alkynide) with terminal alkynes.



White precipitate

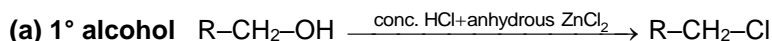
**(ii) Ammonical cuprous chloride (Cu₂Cl₂ + NH₄OH)**

It gives red precipitate with terminal alkynes.

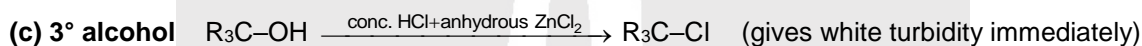
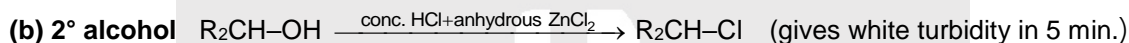
**Section (D) : Tests for alcohols, phenol, nitro group and alkyl halides****D-1 Test for alcohols****(i) Lucas reagent test (Conc. HCl + anhydrous ZnCl₂)**

* It gives white turbidity or cloudiness with alcohols (-OH groups attached with sp³ hybridised carbon).

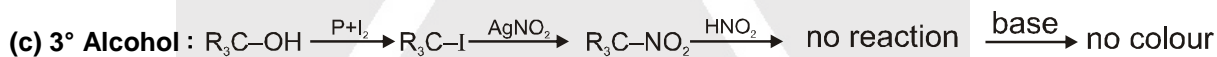
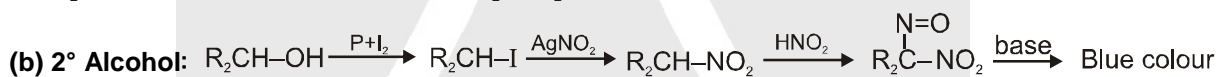
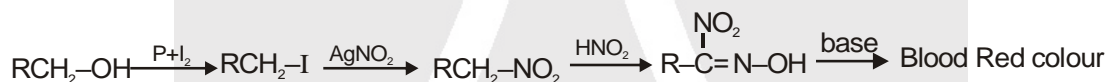
* Lucas Reagent is used to distinguish between 1°, 2°, 3° alcohols because 1°, 2°, 3° alcohols react with different rates.



(Does not give appreciable reaction or gives white turbidity in 30 min.)



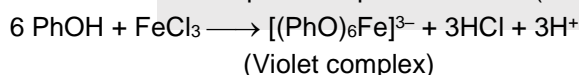
* Phenols and enols do not give Lucas test.

(ii) Victor Mayer test**(a) 1° Alcohol:****(iii) Ceric Ammonium Nitrate test (It is group reagent for alcohols)**

Alcohols(1°,2°,3°) give characteristic red colour with ceric ammonium nitrate (NH₄)₂[Ce(NO₃)₆] solution.

D-2 Neutral FeCl₃ test for phenol or enol

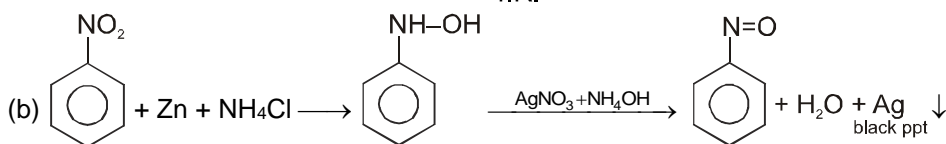
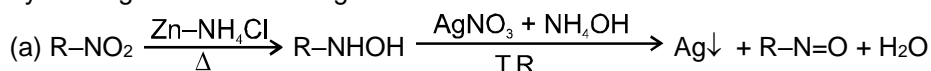
It forms coloured complex with phenol or enol (OH groups attached with sp² carbon).



* Alcohols do not give positive test with FeCl₃.

D-3 Test of nitro group (Mulliken-Barker's test)

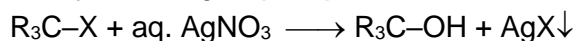
Nitroalkane & nitrobenzene give black precipitate on reduction with Zn and ammonium chloride followed by treating with Tollen's reagent. **This is also said to be Mulliken's test of nitro group.**





D-4 Test for alkyl halides

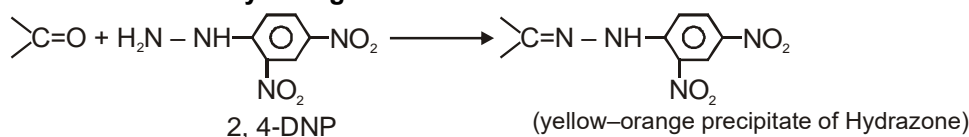
Tertiary halides give precipitate of silver halide with aqueous solution of silver nitrate (AgNO_3).



Section (E) : Tests for aldehydes and ketones (carbonyl compounds)

E-1 2,4-DNP (2, 4-Dinitrophenyl hydrazine) test

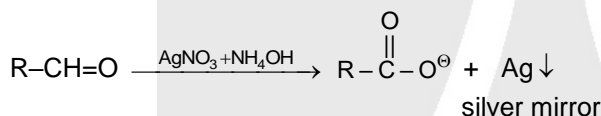
Carbonyl compounds (all aldehydes and ketones) give yellow–orange precipitate with 2,4–DNP. It is also known as **Brady's reagent**.



E-2 Tests for aldehydes

(i) Tollen's reagent [$\text{AgNO}_3 + \text{NH}_4\text{OH}$ or $\{\text{Ag}(\text{NH}_3)_2\}^+ \text{OH}^-$]

Tollen's Reagent gives silver mirror or black precipitate with aldehydes.



Note : α Hydroxy ketones, hemiacetals and formic acid also give Tollen's test.

(ii) Fehling's solution

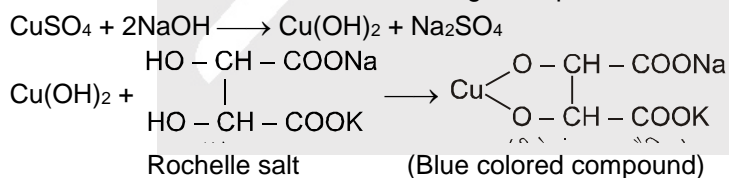
It is an alkaline solution of cupric ion complexed with sodium potassium tartrate.

There are two solutions in Fehling reagent.

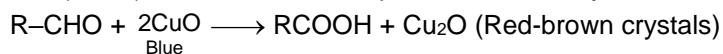
Solution (A) : CuSO_4 solution

Solution (B) : Alkaline solution of sodium potassium tartrate.

When these two solutions are mixed we get deep blue coloured solution.



Equal volume of both the solutions are heated with aldehyde to give red brown crystals of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.

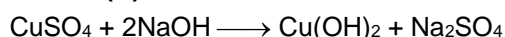


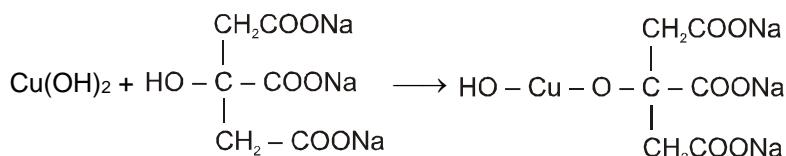
(iii) Benedict's solution

It also consists of two solutions.

Solution (A) : CuSO_4 solution

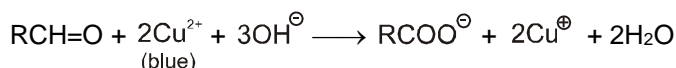
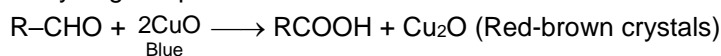
Solution (B) : Alkaline solution of sodium citrate.



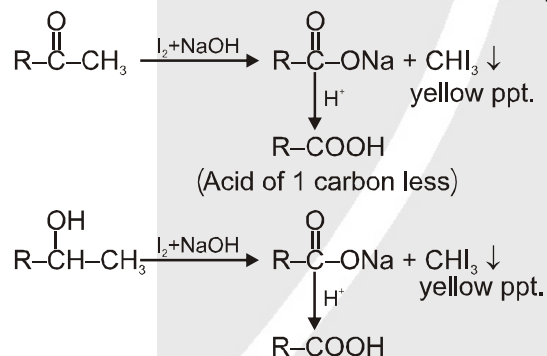
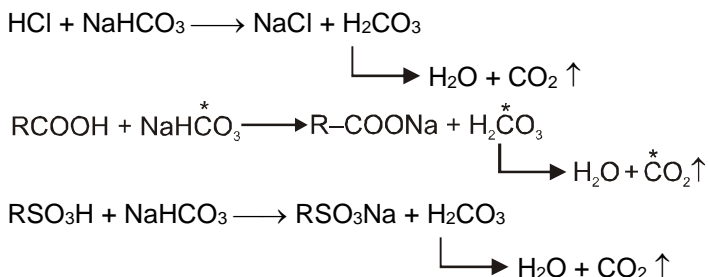


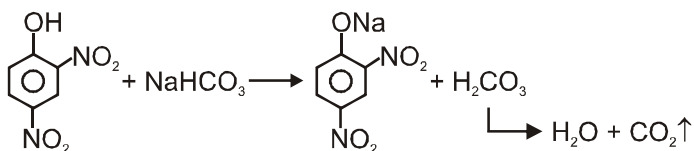
(Blue colour)

Aldehyde gives positive test with Benedict solution.

**Note :** (1) Aromatic aldehydes (Benzaldehyde) do not give Fehling and Benedict test.

(2) If quantity of sugar is less (approximate 1%), then greenish yellow precipitate is obtained rather than red brown precipitate in both Fehling and Benedict tests.

(iv) Schiff's reagentIt is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2 . Aldehyde restores pink colour (Magenta solution in H_2SO_3) when treated with this Schiff's reagent.**E-3 Iodoform test****Reagents :** $\text{I}_2 + \text{NaOH}$ or **NaOI** (Where R = H, alkyl, aryl group)Acetaldehyde ($\text{CH}_3\text{-CH=O}$), all methyl ketones (R-CO-CH_3) & alcohols like R-CH(OH)CH_3 give iodoform test. Acid and acid derivatives do not perform this test.**Section (F) : Tests for acids, esters and amides****F-1 Test for acids****(i) Sodium bicarbonate test (NaHCO_3)**All the acids (carboxylic acids, sulphonic acids, picric acid etc.) which are stronger than H_2CO_3 give effervescence of CO_2 gas with NaHCO_3 .

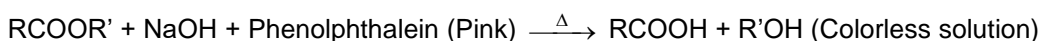


Note : If electron withdrawing group (NO_2) is present at para position of phenol then it gives positive test with sodium bicarbonate.

(ii) **Litmus test :** Acid converts blue litmus into red litmus while base converts red litmus into blue.

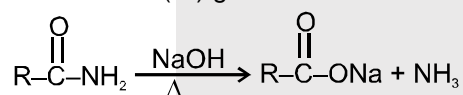
F-2 Test for esters

Esters are sweet (fruity) smelling liquids, when react with NaOH & phenolphthalein then pink colour will disappear on heating.



F-3 Test for acid amide

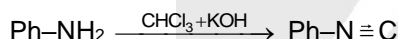
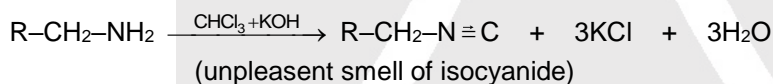
Acid amides (1°) give smell of ammonia when heated with alkali.



Section (G) : Tests for amines

(i) Carbylamines test ($\text{CHCl}_3 + \text{KOH}$)

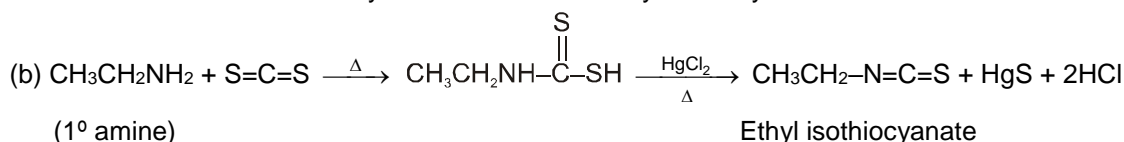
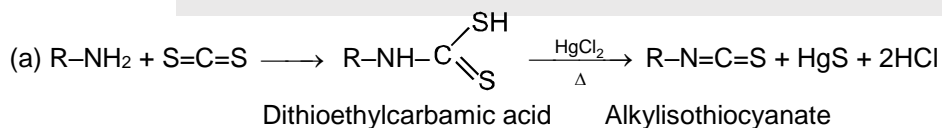
1° Amine (aliphatic and aromatic) give foul smell of isocyanide on reaction with chloroform in alcoholic potash.



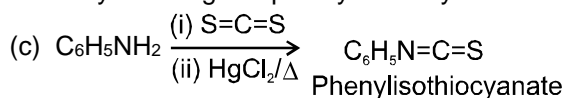
* 2° Amines and 3° Amines do not give this test.

(ii) Hofmann mustard oil test

Primary amines (aliphatic and aromatic both) reacts with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride (HgCl_2) to give alkyl isothiocyanate having smell like mustard oil.



Similarly aniline gives phenylisothiocyanate.

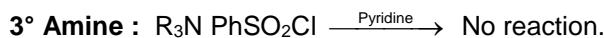
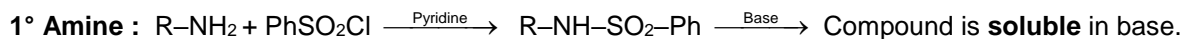


* 2° Amines and 3° Amines do not give this test.



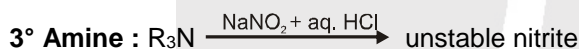
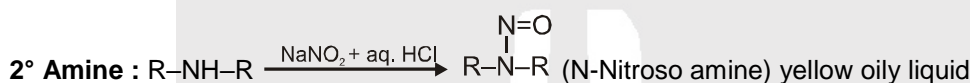
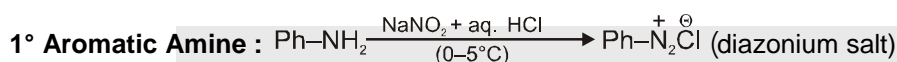
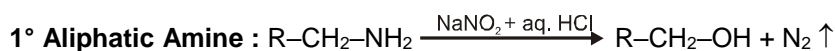
(iii) Hinsberg reagent (C₆H₅SO₂Cl)

This test is used to separate and distinguish between 1°, 2° & 3° amines.



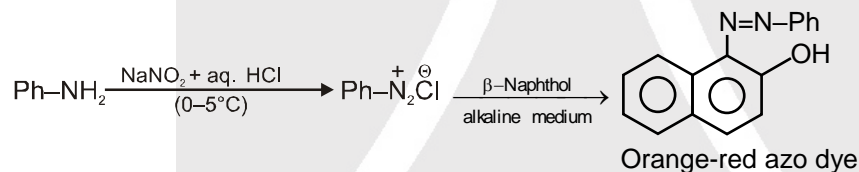
(iv) Sodium nitrite test (NaNO₂ + aqueous HCl)

It is used to distinguish between 1°, 2° and 3° amines and also used to distinguish between aliphatic and aromatic primary amines.



(v) Azo dye test

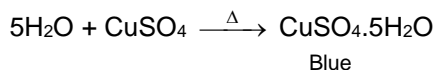
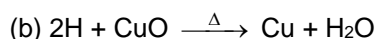
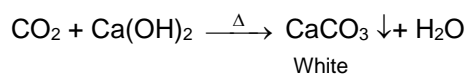
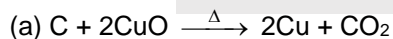
Only 1° aromatic amines give Azo dye test.



Section (H) : Qualitative analysis of elements

H-1 Detection of carbon and hydrogen

Carbon and hydrogen are detected by heating the compound 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).

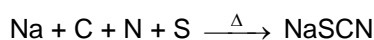
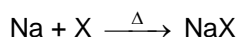
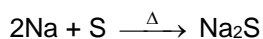


H-2 Detection of other elements by Lassaigne's test

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 their covalent form to their ionic form by fusing the organic compound with sodium metal.

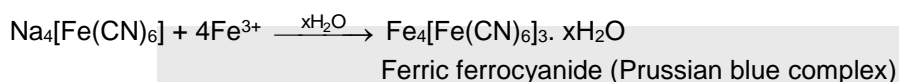
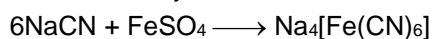


Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as **sodium fusion extract** or **Lassaigne solution**.



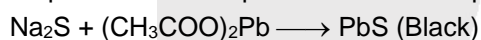
(i) Test for nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with dilute sulphuric acid. The formation of Prussian blue or green colour confirms the presence of nitrogen. Alternatively FeCl_3 and dil. HCl may be added.

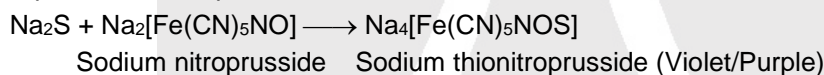


(ii) Test for sulphur

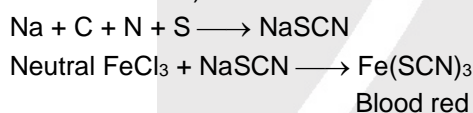
(1) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.



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

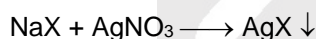


(3) In case, nitrogen and sulphur both are present in an organic compound, then sodium thiocyanate (Blood red colour) is formed with neutral FeCl_3 .



(iii) Test for halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.



(1) White precipitate, soluble in ammonium hydroxide shows the presence of chlorine.

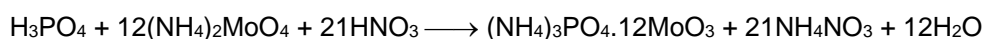
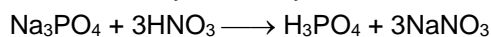
(2) Yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine.

(3) Yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

Note : 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.

(iv) 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 coloration or precipitate indicates the presence of phosphorus.



Ammonium
molybdate

Ammonium
Phosphomolybdate



Section (I) : Quantitative analysis of elements

After the detection of various elements in the organic compounds, the next step is the determination of their percentage composition. The determination of the percentage of various elements is also referred to as **estimation of elements**. The different methods employed for the estimation of various elements are being discussed as below.

I-1 Estimation of carbon and hydrogen (Liebig's method)

Carbon and hydrogen in the organic compound are estimated together by Liebig method.

Principle :

A known mass of the organic compound is heated with dry copper oxide in an atmosphere (or oxygen) free from moisture and carbon dioxide. The carbon and hydrogen of the organic compounds are oxidized to carbon dioxide and water respectively.



Carbon dioxide produced is collected in potash bulbs (containing KOH) whereas water is absorbed in calcium chloride tube (containing CaCl₂). The respective masses of CO₂ and H₂O are determined by difference.

Knowing the masses of CO₂ and water vapors formed and the mass of the compound taken, the percentage of carbon and hydrogen can be calculated.

Calculations :

Let the mass of the organic compound taken = w g

Mass of water formed = x g

(Indicated by increase in the mass of U tube)

Mass of carbon dioxide formed = y g

(Indicated by increase in the mass of potash bulb)

(i) Percentage of Carbon

44 g of CO₂ contains carbon = 12g

y g of CO₂ contains carbon = $\frac{12y}{44}$ g

Now, $\frac{12y}{44}$ g of carbon is present in w g of organic compound.

$$\therefore \text{Percentage of carbon in the organic compound} = \frac{12y}{44 \times w} \times 100$$

(ii) Percentage of Hydrogen

18 g of H₂O contains hydrogen = 2g

x g of H₂O contains hydrogen = $\frac{2x}{18}$ g

Now, $\frac{2x}{18}$ g of hydrogen is present in w g of organic compound.

$$\therefore \text{Percentage of hydrogen in the organic compound} = \frac{2x}{18w} \times 100$$

$$\text{In Short, \%C} = \frac{12 \times W_{\text{CO}_2} \times 100}{44 \times W_{\text{substance}}} \quad \text{and} \quad \text{\%H} = \frac{2 \times W_{\text{H}_2\text{O}} \times 100}{18 \times W_{\text{substance}}}$$



Que. 0.378g of an organic acid gave on combustion 0.264g of carbon dioxide and 0.162g of water vapors. Calculate the percentage of C and H in it.

Ans. Mass of organic compound = 0.378g

Mass of CO₂ formed = 0.264g

Mass of H₂O formed = 0.162g

(i) Percentage of carbon

44g of CO₂ contains carbon = 12g

0.264g of CO₂ contains carbon = $\frac{12}{44} \times 0.264 = 0.072\text{g}$

Percentage of carbon = $\frac{0.072}{0.378} \times 100 = 19.04\%$

(ii) Percentage of hydrogen

18 g of H₂O contains hydrogen = 2g

0.162 g of H₂O contains hydrogen = $\frac{2}{18} \times 0.162 = 0.018\text{g}$

Percentage of hydrogen = $\frac{0.018}{0.378} \times 100 = 4.76\%$

I-2 Estimation of nitrogen

There are two methods for the estimation of nitrogen.

(i) Duma's Method (ii) Kjeldahl's Method

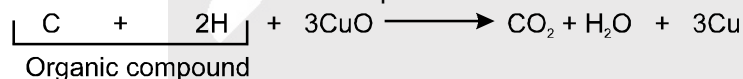
(i) Duma's Method

This method is applicable to nitrogenous compounds.

Principle :

A known mass of the organic compound is heated strongly with excess of copper oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are converted to CO₂ and water. Nitrogen is set free as **dinitrogen**. If any oxide of nitrogen is produced, it is reduced to dinitrogen by passing over hot reduced copper spiral. The dinitrogen is collected over the concentrated solution of potassium hydroxide and its volume is measured at room temperature and atmospheric pressure.

The chemical reaction can be represented as :



Organic compound



(Reduced copper gauze)

Calculations :

Let the mass of the organic compound taken = W g

Volume of moist N₂ collected = v cm³

Barometric pressure = P mm

Room temperature = T K

Pressure of water vapor's at T K = p mm

Pressure of dry N₂ = (P – p) mm





Step I. To find the volume of N_2 to S.T.P.

$$V_1 = v \text{ cm}^3, \quad V_2 = ?, \quad P_1 = (P - p), \quad P_2 = 760 \text{ mm}, \quad T_1 = T, \quad T_2 = 273 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{(P - p)v \times 273}{T \times 760}$$

Step II. Calculation of percentage of nitrogen

22400 cm³ of N_2 at S.T.P. weighs = 28g

Now amount of nitrogen present in W g of organic compound = $\frac{28 V_2}{22400}$ g

$$\text{Percentage of N in organic compound} = \frac{28 V_2}{22400} \times \frac{100}{W}$$

In Short, % N = $\frac{28 \times V_{N_2} (\text{S.T.P.}) \times 100}{22400 \times W_{\text{Substance}}}$

Questions based on Duma's method :

Que. 0.25g of an organic compound gave 30cm³ of moist dinitrogen at 288K and 745mm pressure. Calculate the percentage of nitrogen. (Aqueous tension of 288 K = 12.7mm).

Ans. Mass of the substance = 0.25 g

Volume of moist dinitrogen = 30 cm³

Temperature = 288 K

Pressure = 745 - 12.7 = 732.3 mm

Step I. To find the volume of N_2 at S.T.P.

We know, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$, (P_2, T_2, V_2 refer to S.T.P. conditions)

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{732.3 \times 30 \times 273}{288 \times 760} = 27.4 \text{ cm}^3.$$

Step II. Calculation of percentage of nitrogen.

22400 cm³ of dinitrogen at S.T.P. Weighs = 28 g

27.4 cm³ of dinitrogen at S.T.P. Weighs = $\frac{28 \times 27.4}{22400} = 0.034$ g

Percentage of nitrogen in organic compound = $\frac{0.034}{0.25} \times 100 = 13.6$.

(ii) Kjeldahl's method

This method is simpler and convenient. It is largely used for the estimation of nitrogen in food, fertilizers and drugs. The method is however **not applicable** to compounds containing nitrogen in the ring like **pyridine** or **quinoline** etc, and the compounds, containing **nitro** ($-NO_2$) and **diazo** ($-N = N-$) groups.

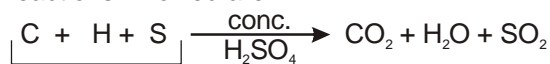
Principle :

A known mass of the organic compound is heated with concentrated sulphuric acid. The nitrogen in the organic compound is quantitatively converted into ammonium sulphate. The resulting liquid is then distilled with excess of sodium hydroxide solution and the ammonia evolved is passed into a known but excess volume of the standard acid (HCl or H_2SO_4). The acid left unused is estimated by titration with some standard alkali. The amount of acid used against ammonia can thus, be known and from this, the percentage of nitrogen in the compound can be calculated.

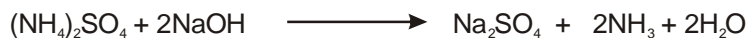
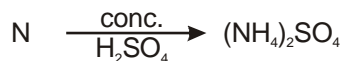




Chemical reactions involved are :



Organic
compound



Calculations :

Let the mass of organic compound = W g

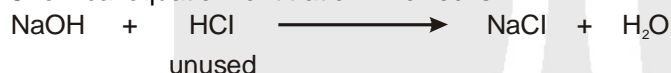
Volume of standard acid (say HCl) taken = V cm³

Let molarity of acid = M₁

Let volume of acid unused be = v₁

Let volume of alkali (say NaOH) of molarity M₂ used for neutralising unused acid = v₂

Chemical equation for titration involved is



∴ According to molarity relation

$$\frac{M_2 v_2}{1} = \frac{M_1 v_1}{1} \quad \text{or} \quad v_1 = \frac{M_2 v_2}{M_1}$$

Volume of acid used by ammonia = (V - v₁) cm³

Millimoles of acid used by ammonia = (V - v₁) × M₁

Millimoles of NH₃ formed = Millimoles of acid used up

$$= (V - v_1) \times M_1$$

Mass of NH₃ formed = Millimoles × 10⁻³ × Molar mass of NH₃

$$= (V - v_1) \times M_1 \times 10^{-3} \times 17 \text{ g}$$

$$\text{Mass of N} = \frac{(V - v_1) M_1 \times 10^{-3} \times 17 \times 14}{17}$$

Mass of N = a g (say)

$$\text{Percentage of N} = \frac{a \times 100}{W}$$

$$\text{In Short} \quad \% \text{ N} = \frac{1.4 \times M_{(\text{acid})} \times \text{basicity of acid} \times V_{(\text{acid used})}}{W_{\text{Substance}}}$$

$$\text{or} \quad \% \text{ N} = \frac{1.4 \times N_{(\text{acid})} \times V_{(\text{acid used})}}{W_{\text{Substance}}}$$

Questions based on Kjeldahl's method :

Que. During nitrogen estimation in an organic compounds by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound neutralised 10 ml, of 1 M H₂SO₄, What is the % of N in the organic compound ?

Ans. Volume of 1 M H₂SO₄ used by NH₃ = 10 ml,

Millimoles of H₂SO₄ used = 10 × 1 = 10 Millimoles

Millimoles of NH₃ produced = 2 × Millimoles of H₂SO₄

$$= 2 \times 10 = 20 \quad (2 \text{ moles of NH}_3 \text{ neutralise 1 mole of H}_2\text{SO}_4)$$



Mass of NH_3 formed = Moles of NH_3 \times Molar mass = $20 \times 10^{-3} \times 17\text{g}$

$$\text{Mass of N} = \frac{20 \times 10^{-3} \times 17 \times 14}{17} = 0.28\text{g}$$

$$\% \text{ of N} = \frac{0.28 \times 100}{0.5} = 56.0\%.$$

I-3 Estimation of halogens by Carius method

Halogen is estimated as silver halides in Carius method.

In the process organic halide is treated with acidified silver nitrate solution to get silver halide which is washed, dried and weighed.

$$\% \text{ X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Wt. of AgX}}{\text{Wt. of organic halide}} \times 100$$

$$\text{Thus, } \% \text{ Cl} = \frac{35.5}{143.5} \times \frac{\text{Wt. of AgCl}}{\text{Wt. of organic halide}} \times 100$$

$$\% \text{ Br} = \frac{80}{188} \times \frac{\text{Wt. of AgBr}}{\text{Wt. of organic halide}} \times 100$$

$$\% \text{ I} = \frac{127}{235} \times \frac{\text{Wt. of AgI}}{\text{Wt. of organic halide}} \times 100$$

I-4 Estimation of sulphur

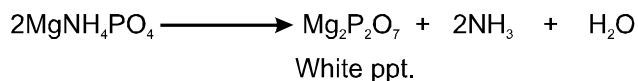
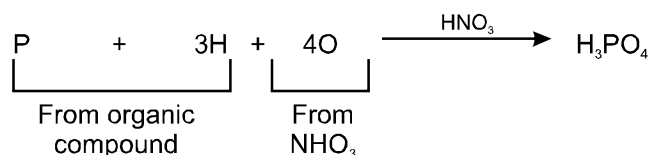
Sulphur is estimated as barium sulphate. In the process organic compound having sulphur is taken in carius tube containing HNO_3 where sulphur is finally converted into sulphuric acid. This sulphuric acid is passed through excess of BaCl_2 to get BaSO_4 which is washed dried & weighed.

$$\% \text{ S} = \frac{\text{Atomic mass of sulphur}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Wt. of BaSO}_4}{\text{Wt. of organic compound}} \times 100$$

$$\% \text{ S} = \frac{32}{233} \times \frac{\text{Wt. of BaSO}_4}{\text{Wt. of organic compound}} \times 100$$

I-5 Estimation of phosphorus

A known mass of the organic compound is heated with fuming nitric acid. The phosphorus present in the organic compound is oxidised to phosphoric acid (H_3PO_4). The phosphoric acid, thus formed is treated with magnesia mixture to get the precipitate of magnesium ammonium phosphate (MgNH_4PO_4). The precipitate is separated, dried and ignited to get magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$). The chemical reactions involved are :



**Calculations :**

Let the mass of the organic compound = W g

Mass of $Mg_2P_2O_7$ obtained = x g

Now, 222 g (G.M.M.) of $Mg_2P_2O_7$ Contains = 62 g phosphorous

x g of $Mg_2P_2O_7$ contains = $\frac{62x}{222}$ g phosphorous

Percentage of P in organic compound = $\frac{62x}{222W} \times 100$

$$\% \text{ of P} = \frac{62 \times W_{Mg_2P_2O_7} \times 100}{222 \times W_{\text{Substance}}}$$

- Que.** (i) In sulphur estimation, 0.157 g of organic compound gave 0.4813 g of $BaSO_4$. What is the percentage of sulphur in organic compound?
 (ii) 0.092 g of organic compound on heating in curius tube and subsequent ignition give 0.111g of $Mg_2P_2O_7$. Calculate the percentage of phosphorus in organic compound.

- Ans.** (i) Mass of $BaSO_4$ = 0.4813g
 Mass of organic compound. = 0.157g

$$\% S = \frac{32 \times W_{BaSO_4} \times 100}{233 \times W_{\text{Substance}}} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10\%$$

- (ii) Mass of organic compound = 0.092g
 Mass of $Mg_2P_2O_7$ = 0.111 g

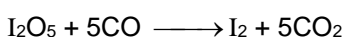
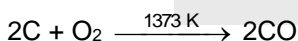
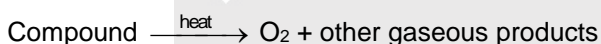
$$\% \text{ of P} = \frac{62 \times W_{Mg_2P_2O_7} \times 100}{222 \times W_{\text{Substance}}} = \frac{62 \times 0.111 \times 100}{222 \times 0.092} = 33.69\%$$

I-6 Estimation of oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements.

However, oxygen can also be estimated directly as below.

A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) where carbon monoxide is oxidised to carbon dioxide and producing iodine.



$$\% \text{ oxygen} = \frac{32 \times m_1 \times 100}{44 \times W}$$

(m_1 = mass of CO_2 and W = mass of sample)

I-7 Estimation of halogen by Beilstein test

A copper wire is cleaned and heated in a Bunsen burner flame to form a coating of copper (II) oxide. It is then dipped in the sample to be tested and once again heated in a flame. A positive is indicated by a **green flame** caused by the formation of a copper halide.

This test does not detect fluorine and fluorides.