NEET | JEE ESSENTIALS

Class XI

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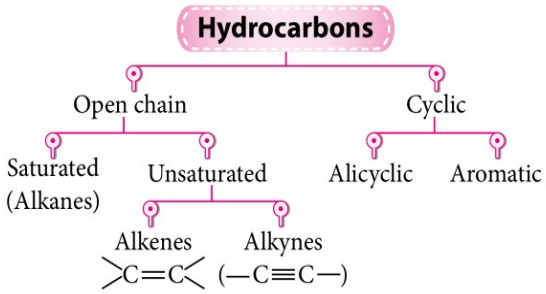
Unit 8

Hydrocarbons | Environmental Chemistry

HYDROCARBONS

INTRODUCTION

Organic compounds composed of only carbon and hydrogen are known as hydrocarbons.



ALKANES

- General formula : C_nH_{2n+2}
- Due to inertness known as paraffins.
- Only C – C and C – H single bonds are present.
- All carbons are sp^3 hybridised.

Isomerism

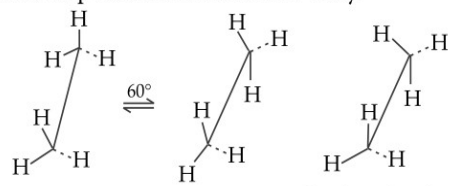
Structural isomerism : Alkanes exhibit only chain isomerism. Methane, ethane, propane do not exhibit isomerism.

Alkane	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
No. of possible isomers	2	3	5	9	18

Conformations

The different arrangements of atoms in space which can be obtained due to rotation about C—C bond are called conformations. To represent these conformations, we can draw three-dimensional pictures. Two simple ways to represent them are :

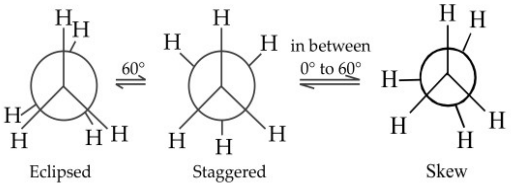
- **Sawhorse projections :** It is a view of molecule at a particular C – C bond and groups connected to both the front and back carbons are drawn using sticks at 120° angle. The left-hand bottom end of this, locates atoms nearer to the observer and right-hand top end atoms are farther away.



Eclipsed form | Staggered form | Gauche or skew form

Sawhorse projections of ethane

- **Newman projections :** In Newman projection, the two carbon atoms forming the σ-bond are represented by two circles, one behind the other, so that only front carbon is seen. The hydrogen atoms attached to the front carbon are shown by the bonds from the centre of the circle while the atoms attached to the back carbon are shown by the bonds from the circumference.



Newman's projections of ethane

Methods of Preparation

1. By hydrogenation of unsaturated hydrocarbons (Sabatier & Senderen's reaction) :

$$C_nH_{2n} + H_2 \xrightarrow[\Delta]{Ni} C_nH_{2n+2}$$

$$C_nH_{2n-2} + 2H_2 \xrightarrow[\Delta]{Ni} C_nH_{2n+2}$$

2. Wurtz reaction :

$$RX + 2Na + XR \xrightarrow[ether]{dry} R - R + 2NaX$$

3. By hydroboration of alkenes :

$$RCH{=}CH_2 \xrightarrow[In\ diglyme]{B_2H_6} (RCH_2CH_2)_3B$$

$$\xrightarrow[NaOH]{AgNO_3} 3RCH_2CH_2CH_2CH_2R$$

4. Corey-House synthesis :

$$RBr + LiR'_2Cu \longrightarrow RR' + R'Cu + LiBr$$

5. Kolbe's electrolysis :

$$2RCOOK + 2H_2O \xrightarrow{electrolysis} R - R + 2CO_2 + 2KOH + H_2$$

6. From Grignard's reagent :

$$RX + Mg \xrightarrow{dry\ ether} R - Mg - X$$

$$R - Mg - X + HOH \xrightarrow{H^+} R - H + Mg\begin{matrix}OH\\X\end{matrix}$$

7. From carbonyl compounds (Clemmensen reduction) :

$$R-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[conc.\ HCl]{Zn/Hg} RCH_2CH_3$$

ALKANE

Chemical Properties

1. Halogenation :

$$CH_4 + 4Cl_2 \xrightarrow{h\nu} CCl_4 + 4HCl$$

2. Nitration :

$$R - H + \underset{(Fuming)}{HONO_2} \xrightarrow[temp.]{high} \underset{Nitroalkane}{R - NO_2} + H_2O$$

3. Sulphonation :

$$R - H + HOSO_3H \xrightarrow[Prolonged\ heating]{SO_3} RSO_3H + H_2O$$

4. Complete combustion :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

5. Incomplete combustion :

$$\underset{(Limited)}{CH_4 + O_2} \xrightarrow{Burn} \underset{black}{C\ (Carbon)} + 2H_2O$$

6. Catalytic oxidation :

$$\underset{9\ :\ 1}{2CH_4 + O_2} \xrightarrow[100\ atm/200°C]{Cu\ tube} 2CH_3OH$$

7. Isomerisation :

$$\underset{n\text{-Butane}}{CH_3(CH_2)_2CH_3} \xrightarrow[200°C,\ 35\ atm]{AlCl_3 + HCl\ (conc.)} \underset{Iso\text{-butane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3}$$

8. Aromatisation :

$$\underset{n\text{-Hexane}}{C_6H_{14}} \xrightarrow[600°C/15\ atm]{Cr_2O_3/Al_2O_3} \underset{Benzene}{\bigcirc} + 4H_2$$

9. Pyrolysis or cracking :

$$CH_4 \xrightarrow{1000°C} C + 2H_2$$

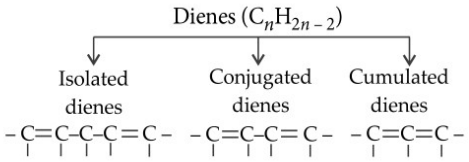
$$C_2H_6 \xrightarrow[Cr_2O_3 + Al_2O_3]{500°C} CH_2{=}CH_2 + H_2$$

Alkenes

- General formula : C_nH_{2n}
- General representation : $RR_1C{=}CR_2R_3$
- Hybridisation (C=C) : sp^2
- Geometry : Planar triangular
- Larger members of the series react with chlorine to form oily products thus, these are also known as olefins.

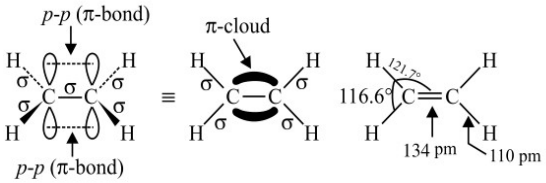
Dienes

Alkenes with two double bonds are known as dienes.



Structure of Double Bond

The C═C bond often known as ethylenic double bond, is made up of a sigma (σ) bond and a pi (π) bond. The sigma bond is a strong bond having bond dissociation enthalpy of about 397 kJ mol^{-1} while pi bond is a weak bond having bond dissociation enthalpy of about 284 kJ mol^{-1}. This is because σ-bond is formed by head on overlapping of orbitals while the π-bond is formed by lateral or sidewise overlapping of the orbitals. Since, extent of overlapping is less in case of π-bond than σ-bond, therefore, a π-bond is weaker bond than a σ-bond.



Methods of Preparation

Dehydration of alcohols — A

$$R{-}OH \xrightarrow[443\,K]{\text{conc. } H_2SO_4}$$

$$R{-}OH \xrightarrow[623\,K-673\,K]{Al_2O_3}$$

Dehydrohalogenation of alkyl halides — L

$$R{-}Br + KOH_{(\text{alc.})} \xrightarrow{\Delta}$$

Dehalogenation of dihalides — K

$$RCH(Br)CH(Br)R \xrightarrow[\text{Ethanol, }\Delta]{Zn/Cu}$$

Partial hydrogenation of alkynes — E, N

$$R{-}C{\equiv}C{-}R \xrightarrow[\text{(Lindlar's catalyst)}]{H_2,Pd/CaCO_3}$$

$$R{-}C{\equiv}C{-}R \xrightarrow[\text{(Birch reduction)}]{Na/\text{liq. } NH_3}$$

Kolbe's electrolytic method — E

$$\begin{matrix}CH_2COONa\\ |\\ CH_2COONa\end{matrix} \xrightarrow{\text{Electrolysis}}$$

Chemical Properties

Alkene

Addition of hydrogen

$$\xrightarrow[523-573\,K]{H_2/Ni,\ Pt,\ or\ Pd} R{-}CH_3$$

Addition of halogens

$$\xrightarrow{Br_2/CCl_4} RCHBrCH_2Br$$

Addition of halogen acids

$$\xrightarrow[(X=Br,Cl,I)]{HX} R{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}CH_3 \quad \text{(Markovnikov's rule)}$$

$$\xrightarrow{HBr/Peroxide} R{-}CH_2{-}CH_2Br \quad \text{(Anti-Markovnikov's rule)}$$

Addition of water (hydration)

$$\xrightarrow{H_2O/H_2SO_4} R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 \quad \text{(Markovnikov's rule)}$$

Hydroboration – oxidation

$$\xrightarrow[H_2O_{2(alk.)}]{B_2H_6} RCH_2CH_2OH$$

Oxymercuration – demercuration

$$\xrightarrow[H_2O]{(CH_3COO)_2Hg/THF} R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

Alkene

Oxidation

$$\xrightarrow[\text{Cold}]{\text{alk. } KMnO_4} RCH(OH){-}CH_2(OH)$$

Ozonolysis

$$\xrightarrow{O_3,Zn/H_2O} RCHO \text{ or } R_2CO$$

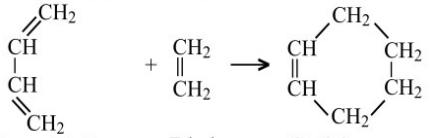
Polymerisation

$$\xrightarrow[1500\ atm,\ 473-673\,K]{\text{Traces of oxygen}} -\left(CH(R){-}CH_2\right)_n-$$

Wacker process

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + PdCl_2 + H_2O \xrightarrow{323\,K} \underset{\text{Acetaldehyde}}{CH_3CHO} + Pd + 2HCl$$

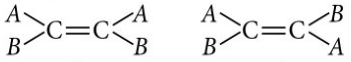
Diels—Alder reaction



Isomerism

Alkenes exhibit the following isomerism :

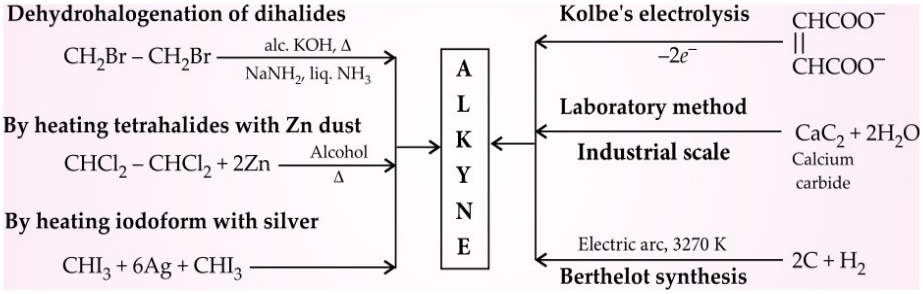
- **Structural isomerism :** Alkenes show chain isomerism (isomers differ with respect to chain of carbon atoms) and position isomerism (isomers differ in the position of the double bond).
- **Geometrical isomerism :** Geometrical isomers are the stereoisomers which have different arrangements of groups or atoms around rigid framework of double bonds. This type of isomerism arises due to restricted rotation around double bond. Isomer in which similar groups or atoms lie on the same side of double bond are called *cis*-isomers whereas isomer in which similar groups or atoms lie on the opposite sides of double bond are called *trans*-isomers.



cis-form *trans*-form

- **Necessary conditions for Geometrical isomerism :**
  - The molecule must have a C=C double bond.
  - Two atoms or groups attached to doubly bonded carbon atoms must be different.

Methods of Preparation

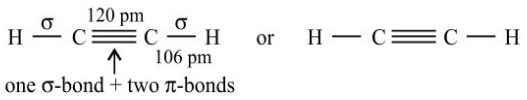


Alkynes

- General formula : C_nH_{2n-2}
- General representation : $R_1C{\equiv}CR_2$
- Hybridisation (C≡C) : *sp*
- Geometry : Linear

Structure of Triple Bond

The simplest member of this homologous series (putting, $n = 2$) has the molecular formula, C_2H_2.



Acidic nature

Alkynes are weakly acidic in nature. As *s*-character increases, acidic nature increases.

	Alkynes	Alkenes	Alkanes	
Hybridisation :	sp	> sp^2	> sp^3	(acidic nature)
s-character :	50%	33.3%	25%	

INFO SHOTS

From C—H to C—C at room temperature!

Recently a new method is devised to selectively introduce aryl groups into C—H bonds at room temperature which is different from conventional idea.

Firstly, iridium catalyst activates C—H containing substrate, then arylsilane attacks the metal creating an intermediate, then oxidation of iridium centre of intermediate causes arylation reaction.

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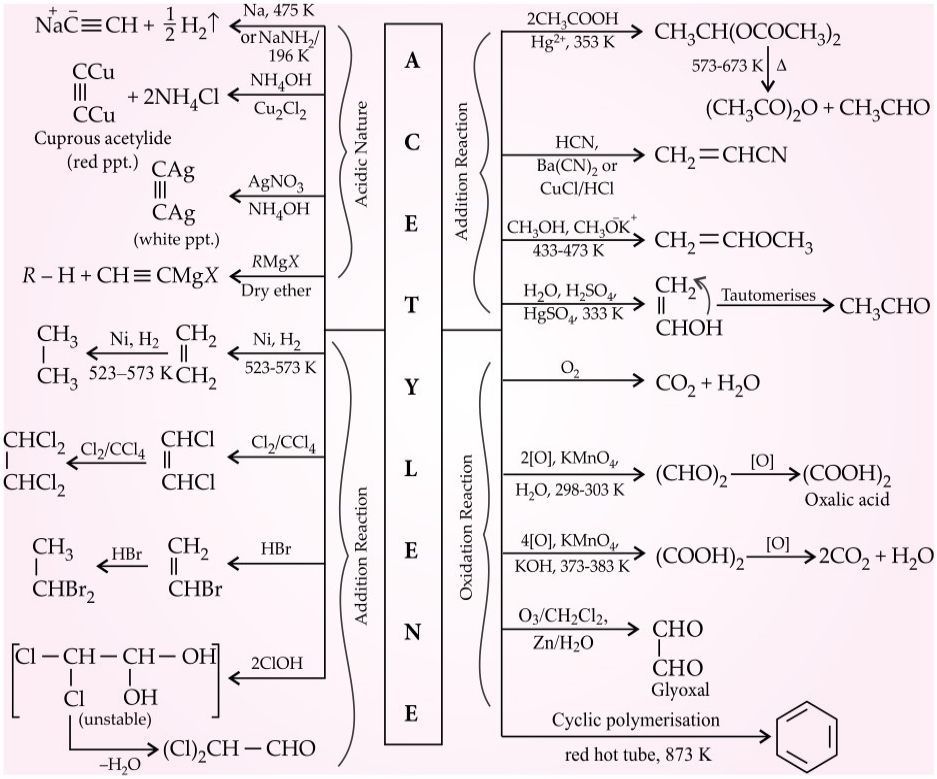
Chemical Properties



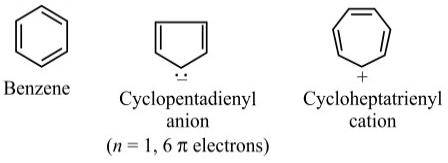
Aromatic Hydrocarbons

- Hydrocarbons with sigma bonds and delocalized pi-electrons between carbon atoms forming a ring.
- They show aromaticity and burn with a sooty flame.
- Carbon-hydrogen ratio is high.
- They undergo electrophilic substitution reactions and nucleophilic aromatic substitutions.

Huckel Rule of Aromaticity

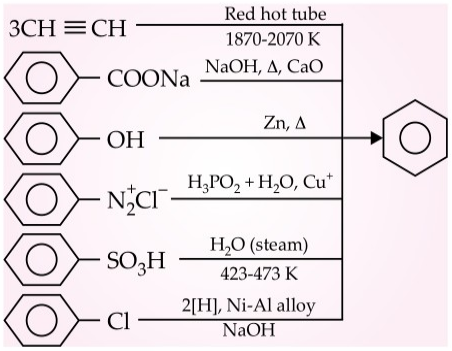
Huckel rule of aromaticity is applied to all the ring systems (whether they have benzene ring or not) which possess the following characteristics :

- Planarity
- Complete delocalisation of π-electrons in the ring.
- Presence of $(4n + 2)\pi$-electrons in the ring where, $n = 0, 1, 2, 3, \ldots$, for example,



Benzene | Cyclopentadienyl anion ($n = 1$, 6 π electrons) | Cycloheptatrienyl cation

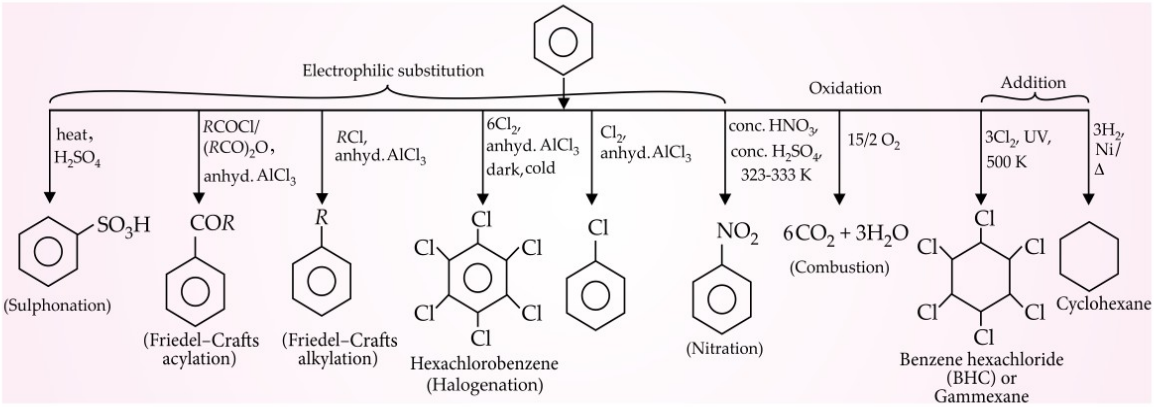
Methods of Preparation



MPP-10 CLASS XI ANSWER KEY

1. (b)	2. (a)	3. (c)	4. (c)	5. (a)
6. (b)	7. (d)	8. (b)	9. (a)	10. (d)
11. (b)	12. (b)	13. (c)	14. (d)	15. (a)
16. (a)	17. (a)	18. (b)	19. (c)	20. (a,b,d)
21. (a,b,c)		22. (a,c)	23. (a,b,c,d)	
24. (3)	25. (3)	26. (4)	27. (c)	28. (b)
29. (b)	30. (c)			

Chemical Properties



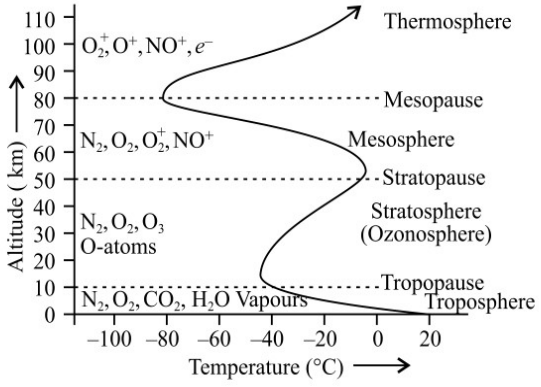
Distinction Tests for Alkanes, Alkenes and Alkynes

	Test	Alkane (ethane)	Alkene (ethene)	Alkyne (ethyne)
1.	Br_2/CCl_4	–	Decolourises. Dibromo derivatives, $C_2H_4Br_2$	Decolourises. Tetrabromo derivatives, $C_2H_2Br_4$
2.	Baeyer's reagent (Alk. $KMnO_4$)	–	Decolourises. $CH_2{=}CH_2 + H_2O + O \rightarrow CH_2OH{-}CH_2OH$	Decolourises. $CH{\equiv}CH + 4[O] \rightarrow COOH{-}COOH$
3.	Ammoniacal Cu_2Cl_2	–	–	Red precipitate
4.	Ammoniacal silver nitrate	–	–	White precipitate

ENVIRONMENTAL CHEMISTRY

Environmental chemistry is the branch of chemistry that deals with the study of various chemical processes taking place in the various segments of the environment.

Regions of the Atmosphere



iNFO SHOTS

First direct proof of ozone hole recovery!

For the first time, scientists have shown through direct satellite observations of the ozone hole that levels of ozone-destroying chlorine are declining (due to international ban on chlorofluorocarbons), resulting in 20 per cent less ozone-depletion during the Antarctic winter than there was in 2005.

Air Pollution

It is the addition of undesirable materials into the atmosphere either due to natural phenomena or due to human activity on the earth which adversely affect the quality of the air and hence, affects the life on the earth.

Pollutants	Major sources	Effects
CO	Incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agricultural and slash matter, volcanic eruptions, forest fires.	Carbon monoxide is toxic. It binds with haemoglobin in red blood cells and prevents them from combining with oxygen. Low levels of CO cause headache and dizziness. Concentration of ~1% causes death in minutes.
NO_x	Combustion of fuel, natural forest fires, stationary combustion sources (factories and power plants), transportation.	Toxic to living tissues, harmful to paints, textiles and metals.
SO_x	Stationary combustion sources, industries involved in metallurgy, coal, decay products, volcanoes.	They are respiratory tract irritants, low concentration causes throat, eye irritation and breathlessness, affect larynx.
Hydrocarbons	Combustion of fuel in automobiles, refineries, anaerobic bacterial decomposition of organic matter, natural gas.	At concentration greater than 500–1000 ppm, they have carcinogenic effect in lungs. They react with O_2 and NO_x to form photochemical smog which have a strong damaging effect on human beings as well as on plants.
CFC's	CFC's were used primarily as refrigerants, in aerosol sprays and in the plastic industry. Freons are stable (lasts for over 80 years), inflammable and inert (in the lower atmosphere).	React with stratospheric ozone. When CFC's are broken down, chlorine free radicals are produced. These can react with more than 10,000 molecules of ozone thus, depleting the ozone layer.
Particulates	Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers and grinders.	Inhalation of metallic particles leads to respiratory disorders like asthma, bronchitis, lung cancer, etc.

Smog

- The word smog is derived from smoke and fog. It is the major air pollutant.

  Smoke + Fog (containing harmful gases) $\longrightarrow$ Smog

- Smog is of two types :

Classical smog	Photochemical smog
Also called as London smog.	Also called as Los Angeles smog.
Formed due to oxides of sulphur.	Formed due to oxides of nitrogen.
Contains primary pollutants.	Contains secondary pollutants.
Causes bronchitis and problems in lungs.	Causes irritation in eyes.
It is reducing in nature.	It is oxidising in nature.

Stratospheric Pollution

Ozone depletion : The ozone layer existing between 15 to 25 km above the earth's surface, shield the earth from the harmful UV radiations from the sun. The UV radiations cause skin cancer, eye cataract, and harmful to vegetation.

- Depletion of ozone is caused by oxides of nitrogen :

$$N_2O + h\upsilon \longrightarrow \underset{\text{(Reactive)}}{NO} + N$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$O_3 + h\upsilon \longrightarrow O_2 + O$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$2O_3 + h\upsilon \longrightarrow 3O_2 \text{ (Net reaction)}$$

- The presence of oxides of nitrogen increase the decomposition of O_3.
- Depletion of ozone by chlorofluorocarbons :

$$CF_2Cl_2 + h\upsilon \longrightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$
$$CFCl_3 + h\upsilon \longrightarrow CFCl_2^{\bullet} + \underset{\text{(Reactive)}}{Cl^{\bullet}}$$
$$\dot{Cl} + O_3 \longrightarrow Cl\dot{O} + O_2$$
$$Cl\dot{O} + O \longrightarrow \dot{Cl} + O_2$$
$$O_3 + O \longrightarrow 2O_2 \text{ (Net reaction)}$$

Greenhouse Effect and Global Warming

The retention of heat by the earth and atmosphere from the sun and its prevention to escape into the outer space is known as greenhouse effect.

- Greenhouse gases such as CO_2, ozone, methane, chlorofluorocarbons and water vapours form a thick cover around the earth which prevents the IR rays emitted by the earth to escape.
- It gradually leads to increase in temperature of atmosphere. This phenomenon of increasing earth's temperature is called global warming.
- The relative contribution of different greenhouse gases :
  CO_2(50%), CH_4(19%), CFC's(17%), O_3(8%), N_2O(4%), H_2O(2%)

Methods to prevent global warming

- By minimising uses of cars.
- By plantation.
- By avoiding burning of dry leaves, etc.

Acid Rain

- The oxides of C, N and S present in the atmosphere, dissolve in water and produce acids which lower the pH of rain water below 5.6. This is known as acid rain.
- The acids are toxic to vegetation, react with marble and damage buildings, corrode water pipes and produce salts with heavy metal ions *viz.*, Cu, Pb, Hg and Al which are toxic in nature.

Water Pollution

- Water pollution is defined as, the contamination of water by foreign substances which makes it harmful for health of animals, plants or aquatic life and makes it unfit for domestic, industrial and agricultural use.

Pollutants	Major sources
Natural wastes	Leaching of minerals, silt from soil erosion, falling of organic matter from banks, etc.
Organic chemicals	Pesticides, surfactants, detergents, industrial wastes.
Metals (Hg, As, Pb, Cd, etc.)	Nuclear power plants, mining, metal plating industries.
Man-made wastes	Sewage, domestic wastes, soaps and detergents, wastes from animal sheds and slaughter houses, run off from agricultural fields, industrial wastes.

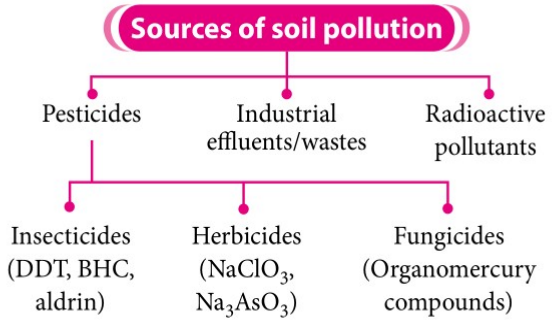
- **Biochemical Oxygen Demand (BOD) :** It is defined as, the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days. Its unit is mg/L or ppm. An average sewage has BOD value of 100 to 150 mg/L.
- **Chemical Oxygen Demand (COD) :** It is measure of all types of oxidisable impurities (biologically oxidisable and biologically inert organic matter such as cellulose) present in the sewage. COD values are higher than BOD values.

Eutrophication

- Eutrophication is a process whereby water bodies, receive excess nutrients that stimulate excessive plant growth (algae, periphyton attached algae and other plant weeds). This enhanced plant growth, often called an algal bloom, reduces dissolved oxygen in the water.

Soil Pollution

- The addition of substances in an indefinite proportion changing the productivity of the soil is known as soil pollution.



Effects of Soil Pollution

- Pollution runs-off into rivers and kills the fishes, plants and other aquatic life.
- Contaminated soil decreases soil fertility and hence, there is decrease in the crop yield.
- People living near polluted land tend to have higher incidences of migraine, nausea, fatigue, skin disorders and even miscarriages.

Control of Soil Pollution

- Reuse and recycle unwanted items.
- Make use of organic fertilizers and organic pesticides because they are usually made of natural substances so, are biodegradable.
- Cut down the usage of paper or use recycled paper.

Control of Environmental Pollution

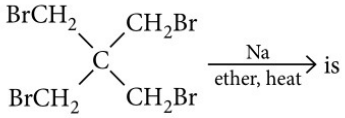
- **Waste management :** Environmental pollution can be controlled to a certain extent by managing the waste disposal in a proper way.
- **Recycling :** A large amount of disposed waste material can be reused by recycling the waste. Thus, it reduces the land fill and converts waste into usable forms.
- **Incineration :** Incineration is a waste treatment technology that involves the combustion of organic materials and/or substances. Incineration of waste materials converts the waste into ash, flue gases particulates and heat, which can in turn be used to generate electricity. Incinerators reduce the volume of the original waste by almost 95%.

Green Chemistry

- Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous susbtances.
- Green chemistry refers to the redesign of chemical products and processes with the goal of reducing or eliminating any negative environmental or health effects. Examples of green chemistry projects include : finding non-toxic, non-volatile solvent substitutes, developing new catalysts and environmental friendly materials.

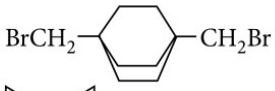
SPEED PRACTICE

1. The product formed in the reaction,



(a) $(BrCH_2)_3CCH_2CH_2C(CH_2Br)_3$

(b) 

(c) 

(d) 

2. 5 L aqueous solution is kept in the presence of oxygen and suitable microorganism for five days at 20 °C. If the O_2 consumed is 0.2 g, the BOD value of the sample is

(a) 4 ppm (b) 0.4 ppm (c) 40 ppm (d) 20 ppm

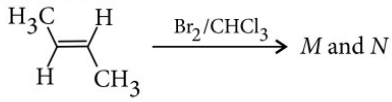
3. Which of the following reacts with $KMnO_4$ but does not react with $AgNO_3$?

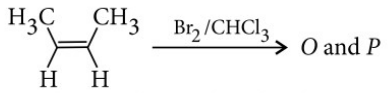
(a) C_2H_6 (b) CH_4 (c) C_2H_4 (d) C_2H_2

4. Peeling of ozone umbrella is due to

(a) CFCs (b) PAN
(c) CO_2 (d) coal burning.

5. The correct statement(s) for the following addition reactions is(are)

(i) 

(ii) 

(a) *O* and *P* are identical molecules
(b) bromination proceeds through *trans*-addition in both the reactions
(c) (*M* and *O*) and (*N* and *P*) are two pairs of enantiomers
(d) (*M* and *O*) and (*N* and *P*) are two pairs of diastereomers. **(JEE Advanced 2017)**

6. The correct reactivity order of the labelled bonds towards Br^+ is