B.Sc. I

Paper II Organic Chemistry

ELECTROPHLIC SUBSTITUTION
FREE RADICAL SUBSTITUTION

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ELECTROPHILIC SUBSTITUTION

What is an Electrophilic Substitution Reaction?

An Electrophilic Substitution reaction is a chemical reaction in which the functional group attached to a compound is replaced by an Electrophile [$\mathbf{E}^+$].

The displaced/replaced functional group is typically a hydrogen atom.

Electrophilic substitution reactions generally proceed via a three-step mechanism that involves the following steps:

1. **The generation of an electrophile.**
2. **The formation of a carbocation (which is an intermediate).**
3. **The removal of a proton from the intermediate.**

TYPES OF ELECTROPHILIC SUBSTITUTION

1. Electrophilic Aromatic Substitution Reaction

In electrophilic aromatic substitution reactions, an atom (hydrogen, H^+) attached to an aromatic ring is replaced with an electrophile (E^+).

Examples :

Aromatic nitration, Aromatic sulphonation, and Friedel-Crafts reactions.

2. Electrophilic Aliphatic Substitution Reaction

In electrophilic aliphatic substitution reactions, an electrophile (E^+) replaces the functional group (H^+) in an aliphatic compound.

Examples:

Halogenation of ketones

Tautomerism

ELECTROPHILIC AROMATIC SUBSTITUTION

1. GENERATION OF ELECTROPHILE

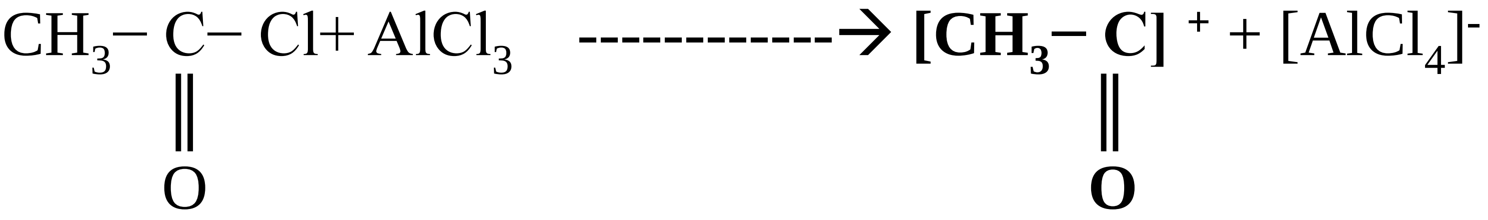
Anhydrous AlCl3 is a good Lewis acid in generating and electrophile from chlorine, alkyl halide and acid chloride for aromatic halogenation, aromatic alkylation and aromatic acylation respectively.
[Friedel Crafts reactions of benzene]

$$\mathrm{Cl{-}\,Cl + AlCl_3} \;\text{------------}\!\!\rightarrow\; \mathbf{[Cl]}^{+} + [\mathrm{AlCl_4}]^{-}$$

(aromatic halogenation)

$$\mathrm{CH_3{-}\,Cl + AlCl_3} \;\text{------------}\!\!\rightarrow\; \mathbf{[CH_3]}^{+} + [\mathrm{AlCl_4}]^{-}$$

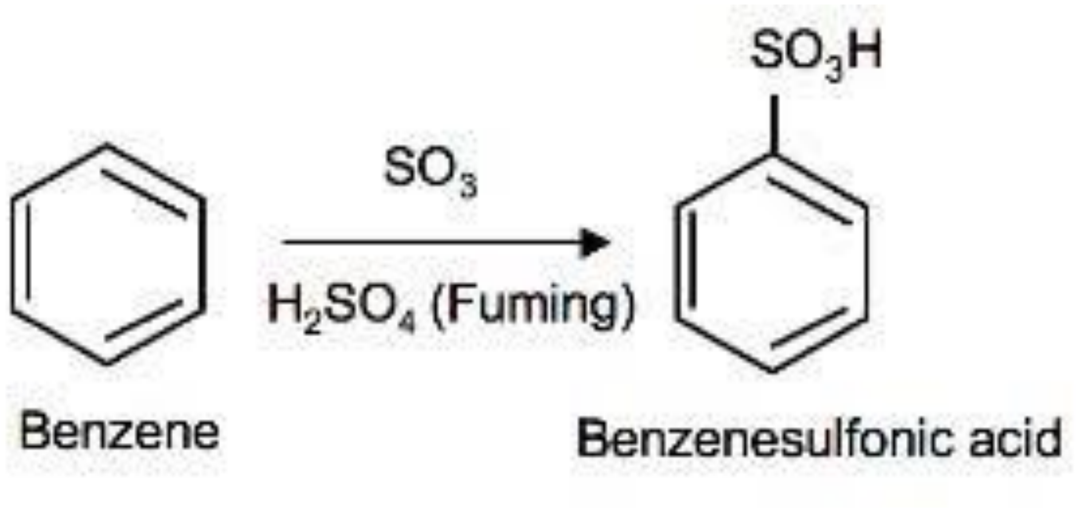
(aromatic alkylation)



$$\mathrm{CH_3{-}\,\underset{\underset{O}{\|}}{C}{-}\,Cl + AlCl_3} \;\text{------------}\!\!\rightarrow\; \mathbf{[CH_3{-}\,\underset{\underset{O}{\|}}{C}]}^{+} + [\mathrm{AlCl_4}]^{-}$$

(aromatic acylation)

ELECTROPHILIC AROMATIC SUBSTITUTION

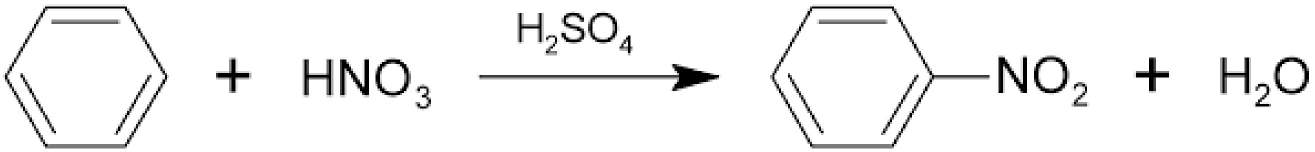


Sulphonation of benzene is a reversible reaction that produces benzene sulphonic acid by substitution of hydrogen atom of benzene ring by electrophile sulphur trioxide.

SO_3 is produced from concentrated sulphuric acid.

$$2H_2SO_4 == [H_3O]^+ + [HSO_4]^- + [SO_3]$$

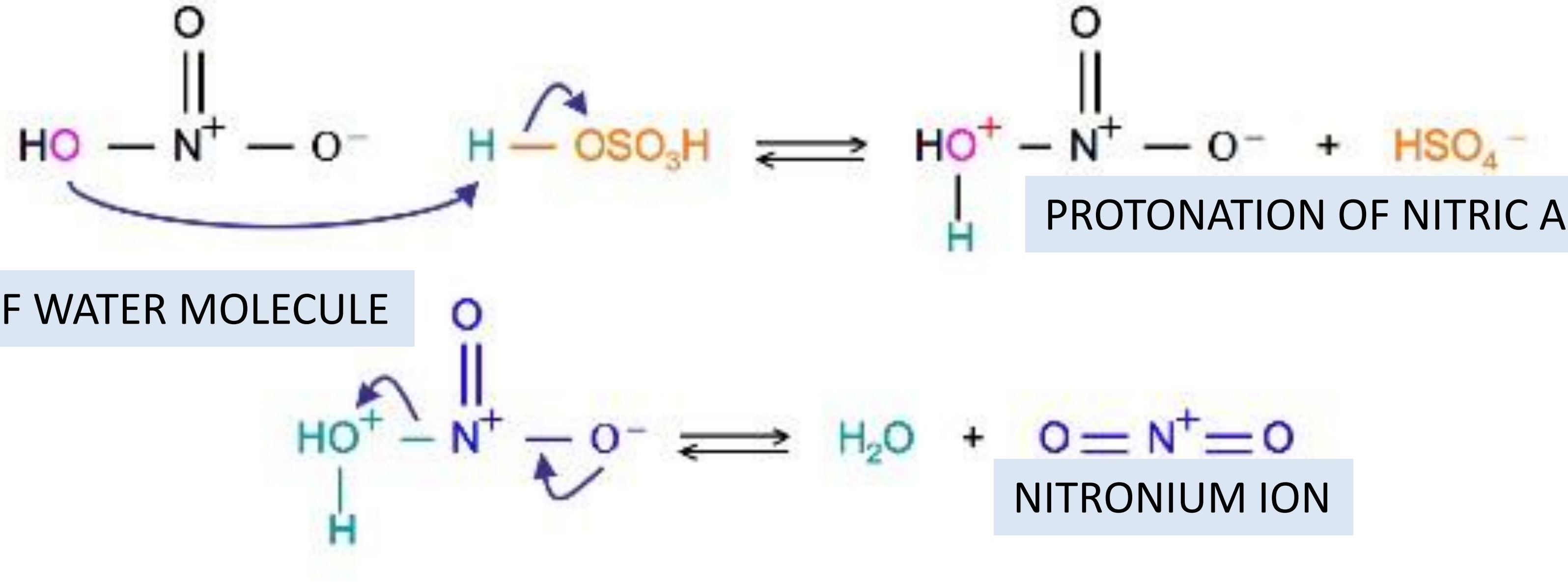
Electrophilic Aromatic Substitution – Nitration of Benzene



Nitration of benzene occurs when one (or more) of the hydrogen atoms on the benzene ring is replaced by a **nitro group, NO_2**.

Concentrated sulphuric acid and concentrated nitric acid are used to make a nitration mixture.

This nitration mixture generates Nitronium $[NO2]^+$ electrophile for aromatic nitration.



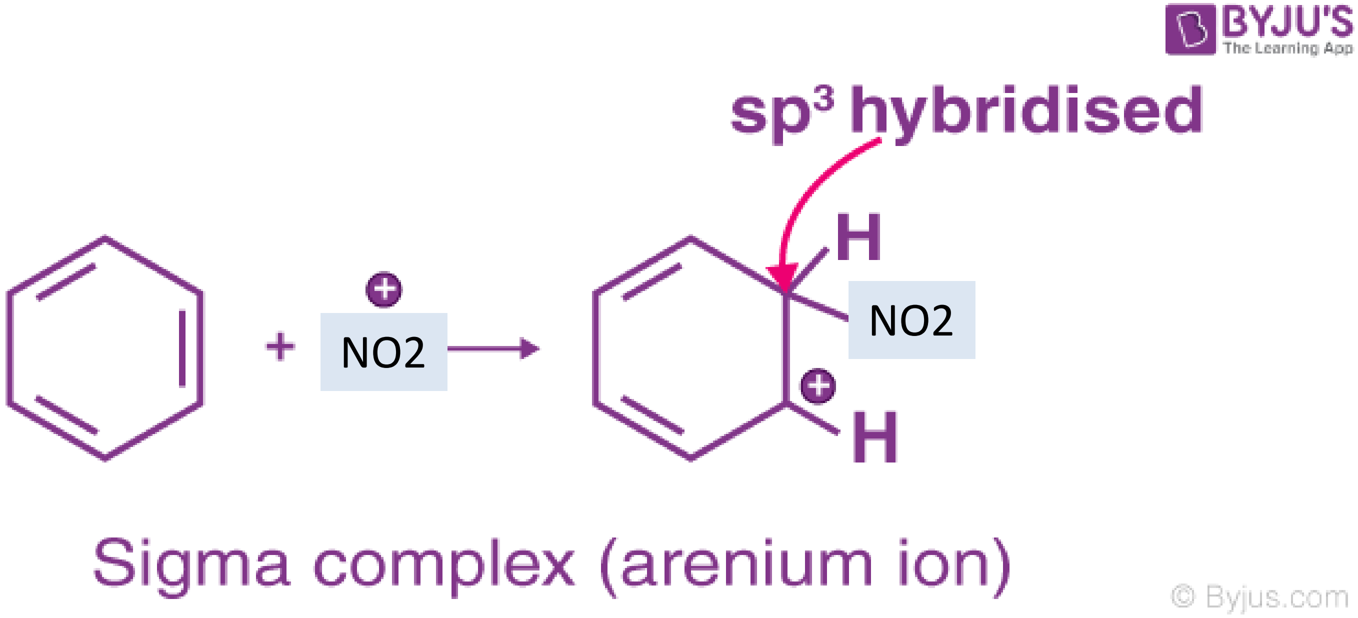
PROTONATION OF NITRIC ACID

LOSS OF WATER MOLECULE

NITRONIUM ION

NITRATION OF BENZENE

2. FORMATION OF CARBOCATION:



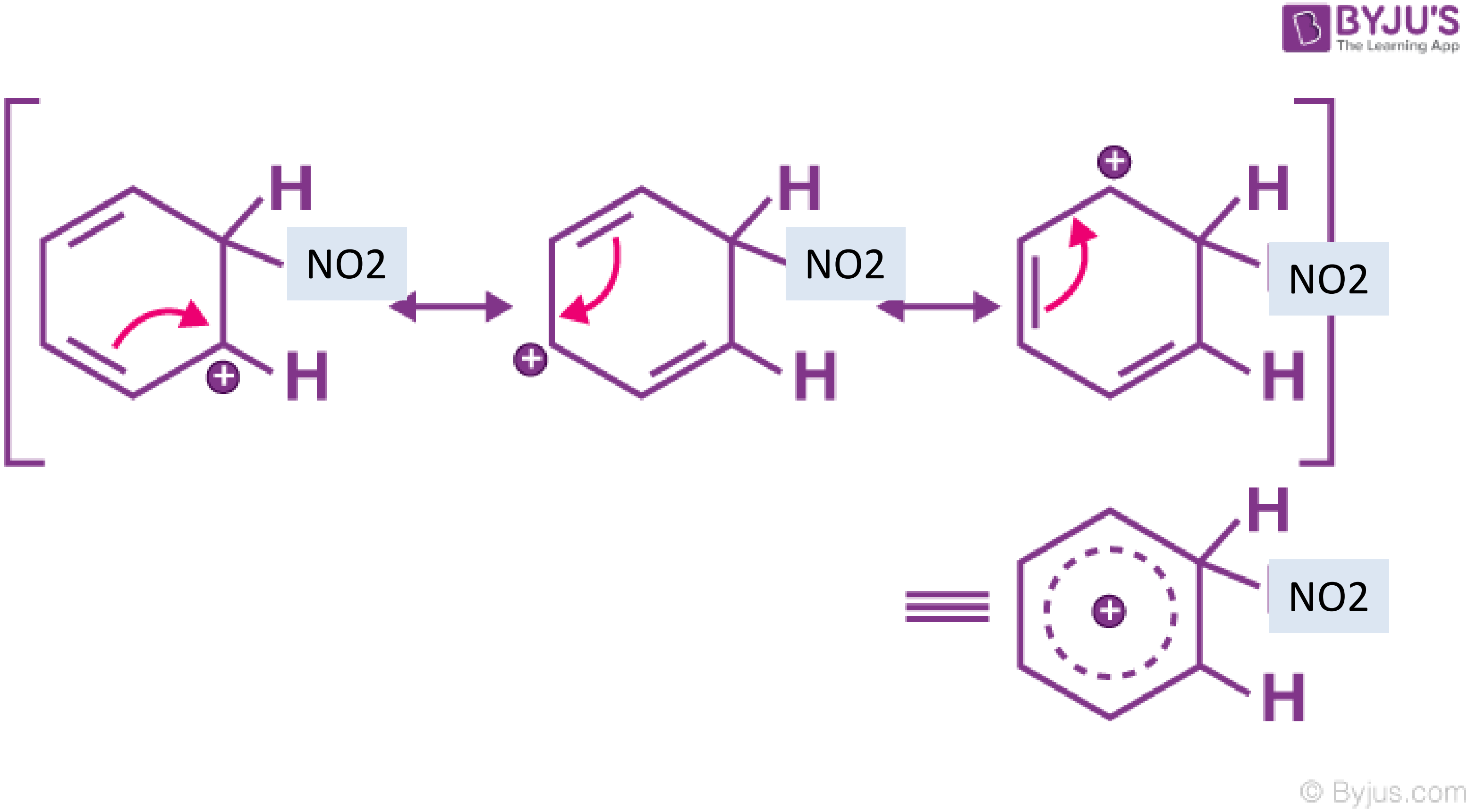
The Nitronium ion, $[NO2]^{+}$ (electrophile) attacks the aromatic ring, forming a **sigma complex or an arenium ion**.

One of the carbons in this arenium ion is sp^3 hybridized.

NITRATION OF BENZENE

This arenium ion is stabilized due to resonance.

The delocalization of electrons stops at the sp^3 hybridized carbon and the sigma complex or the arenium ion loses its aromatic character.

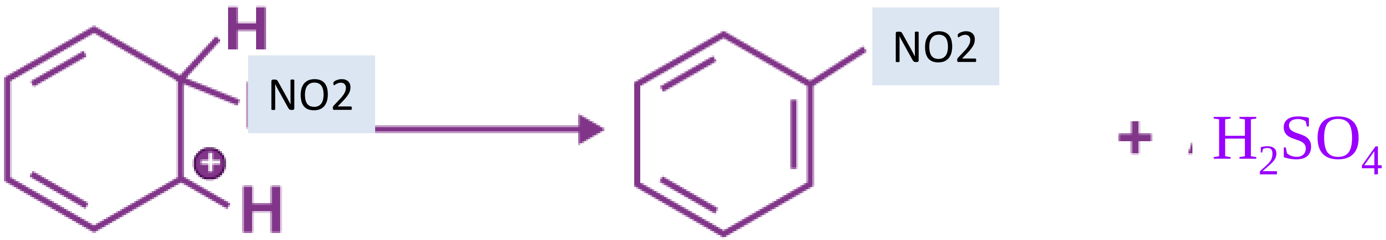


NITRATION OF BENZENE

3. REMOVAL OF PROTON FROM BENZENE

In order to restore the aromatic character, the sigma complex releases a proton from the sp^3 hybridized carbon when it is attacked by the, HSO_4^- or $[AlCl_4]^-$.

The reaction describing the removal of a proton from the sigma complex is given below:



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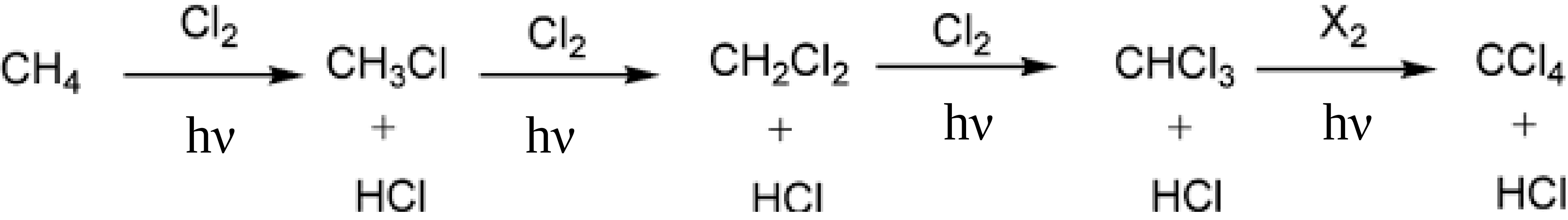
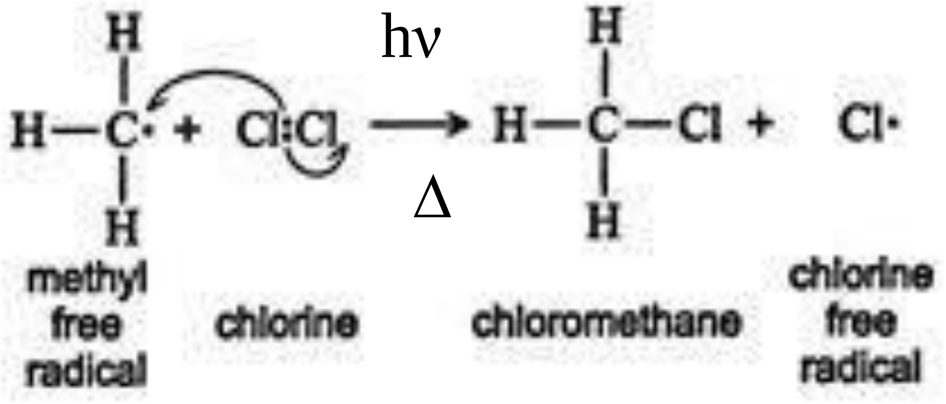
FREE RADICAL SUBSTITUTION

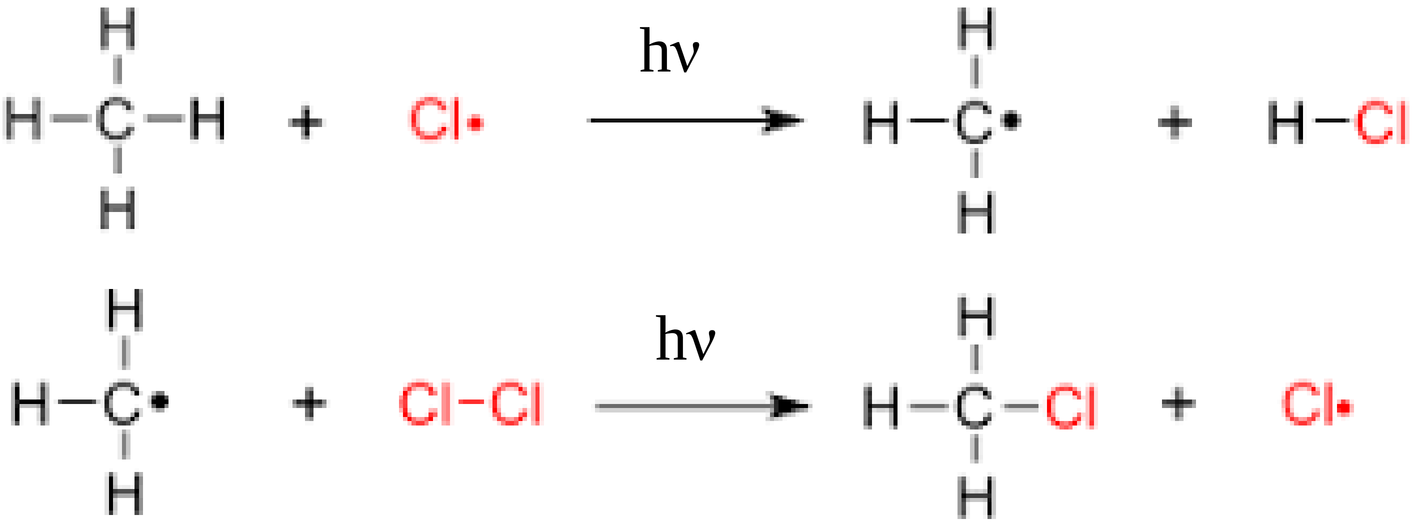
Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms. Alkanes are notoriously unreactive compounds because they are non-polar and lack functional groups at which reactions can take place.



HALOGENATION OF ALKANES



$$H_3C\cdot + Cl{:}Cl \xrightarrow[\Delta]{h\nu} H_3C\text{-}Cl + Cl\cdot$$

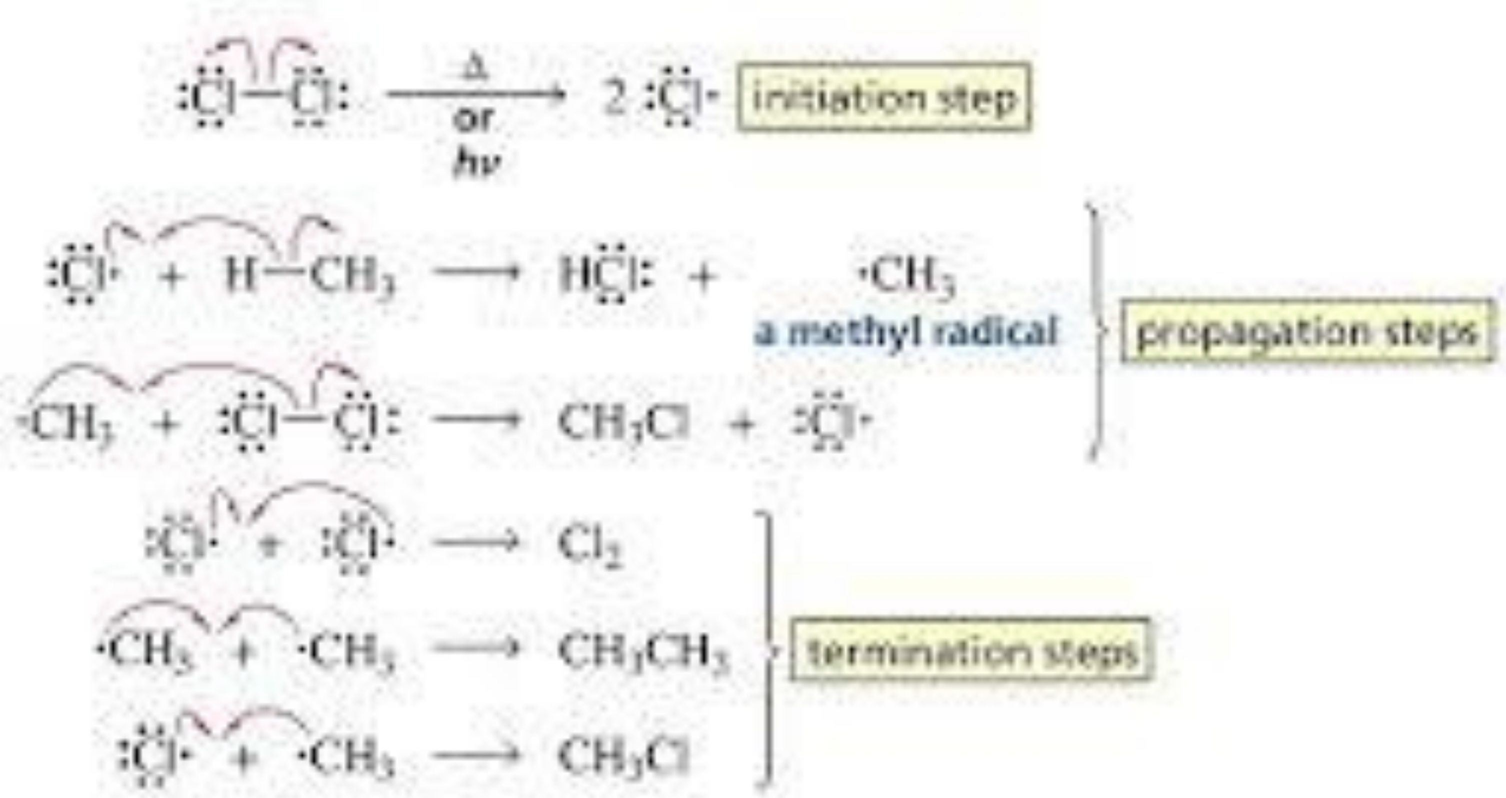


$$CH_4 + Cl\cdot \xrightarrow{h\nu} CH_3\cdot + H\text{-}Cl$$

$$CH_3\cdot + Cl\text{-}Cl \xrightarrow{h\nu} CH_3\text{-}Cl + Cl\cdot$$

HALOGENATION OF ALKANES

mechanism for the monochlorination of methane



$$Cl{-}Cl \xrightarrow[\text{or } h\nu]{\Delta} 2\,Cl\cdot$$

$$Cl\cdot + H{-}CH_3 \longrightarrow HCl + \cdot CH_3$$

$$\cdot CH_3 + Cl{-}Cl \longrightarrow CH_3Cl + Cl\cdot$$

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$$

$$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$