Unsaturated halides (Halo-alkene).

Vinyl chloride or chloroethene,CH_2=CHCl

(1)**Synthesis:**Vinyl chloride can be synthesized by a number of methods described below:

(i) **From ethylene chloride**: It is easily prepared in the laboratory by the action of dilute alcoholic solution of potassium hydroxide on ethylene chloride.

$$\underset{\text{Ethylene chloride}}{\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}} \xrightarrow[\text{+ Alc. KOH}]{} \underset{\text{Vinyl chloride}}{\begin{matrix}CHCl\\||\\CH_2\end{matrix}} + KCl + H_2O$$

Vinyl chloride can also be obtained from ethylene chloride by thermal decomposition at 600-650°C.

$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} \longrightarrow \begin{matrix}CHCl + HCl\\||\\CH_2\end{matrix}$$

(ii) **From ethylene**: Free radical chlorination of ethylene at 500°C yields vinyl chloride.

$$CH_2 = CH_2 + Cl_2 \xrightarrow{500\,^\circ C} \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$

(iii) **From acetylene**: Vinyl chloride is obtained by controlled addition of HCl on acetylene. Acetylene is passed through dilute hydrochloric acid at about 70°C in presence of $HgCl_2$ as a catalyst to form vinyl chloride. This method is also used for its manufacture.

$$CH \equiv CH + HCl \xrightarrow[70\,^\circ C]{HgCl_2} \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$

(2) **Properties:** It is a colorless gas at room temperature. Its boiling point is –13°C. The halogen atom in vinyl chloride is not reactive as in other alkyl halides. However, $C = C$ bond of vinyl chloride gives the usual addition reactions.

The non-reactivity of chlorine atom is due to resonance stabilization. The lone pair on chlorine can participate in delocalization (Resonance) to give two structures.

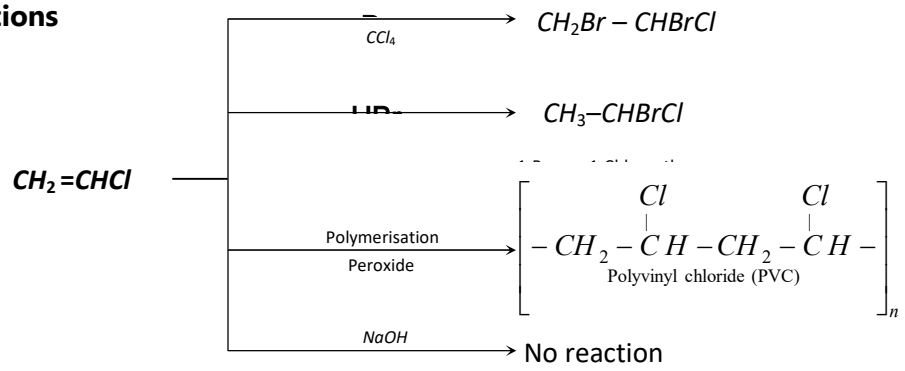
$$\underset{\text{(i)}}{CH_2 = CH - \ddot{Cl}} \longleftrightarrow \underset{\text{(ii)}}{\overset{-}{C}H_2 - CH = \overset{+}{C}l}$$

The following two effects are observed due to resonance stabilization.

(i) Carbon-chlorine bond in vinyl chloride has some double bond character and is, therefore, stronger than a pure single bond.

(ii) Carbon atom is sp^2 hybridized and $C-Cl$ bond length is shorter (1.69Å) and stronger than in alkyl halides (1.80Å) due to sp^3 hybridization of the carbon atom.

Addition reactions



(3) **Uses:**The main use of vinyl chloride is in the manufacture of polyvinyl chloride **(PVC)** plastic which is employed these days for making synthetic leather goods, rain coats, pipes, floor tiles, gramophone records, packaging materials, etc.

Allyl iodide or 3-iodopropene-1, $ICH_2CH = CH_2$

(1) **Synthesis:**It is obtained,

(i) By heating allyl chloride with sodium iodide in acetone. Allyl chloride required in the reactions is prepared either by chlorination of propene at 500°C or by action of PCl_3 on allyl alcohol.

$$\underset{\text{Propene}}{CH_3CH=CH_2} + Cl_2 \xrightarrow{500^\circ C} \underset{\text{Allyl chloride}}{\underset{Cl}{\underset{|}{CH_2}}-CH=CH_2}$$

Or $$3\underset{OH}{\underset{|}{CH_2}}-CH=CH_2 + PCl_3 \xrightarrow{\text{Heat}} 3\underset{Cl}{\underset{|}{CH_2}}-CH=CH_2 + H_3PO_3$$

Allylalcohol

$$\underset{Cl}{\underset{|}{CH_2}}-CH=CH_2 + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} \underset{I}{\underset{|}{CH_2}}-CH=CH_2 + NaCl$$

Allylchloride Allyliodide

This is halogen- exchange reaction and is called **Finkelstein reaction**.

(ii) By heating glycerol with HI.

$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}} + 3HI \xrightarrow[-3H_2O]{} \underset{\text{1,2,3 - Tri-iodopropan e}}{\begin{matrix}CH_2I\\|\\CHI\\|\\CH_2I\end{matrix}} \xrightarrow[-I_2]{\text{Heat}} \underset{\text{Allyliodide}}{\begin{matrix}CH_2I\\|\\CH\\\|\\CH_2\end{matrix}}$$

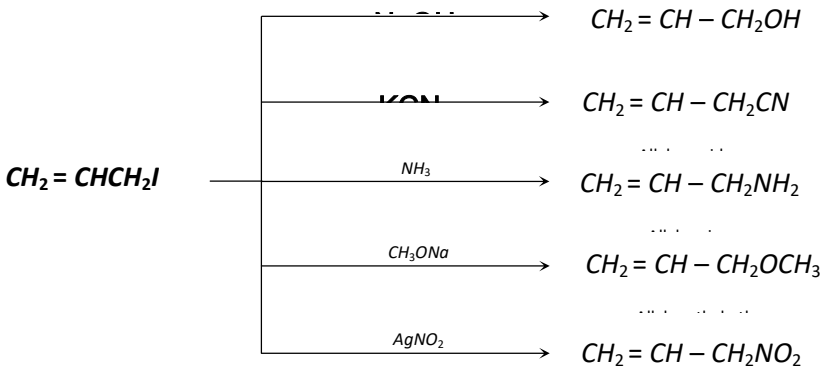
(2) **Properties:**It is a colorless liquid. It boils at 103.1°C.The halogen atom in allyl iodide is quite reactive. The p-orbital of the halogen atom does not interact with π-molecular orbital of the double bond

because these are separated by a saturated sp^3 -hybridized carbon atom. Thus, the halogen atom in allyl halides can be easily replaced and the reactions of allyl halides are similar to the reaction of alkyl halides.

In terms of valence bond approach, the reactivity of halogen atom is due to ionisation to yield a carbonium ion which can stabilize by resonance as shown below,

$$CH_2 = CH - CH_2I \longrightarrow [CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2] + I^-$$

Substitution reactions: Nucleophilic substitution reactions occur,



Addition reactions: Electrophilic addition reactions take place in accordance to Markownikoff's rule.

$$CH_2 = CH - CH_2I + Br_2 \longrightarrow \underset{1,2-\text{Dibromo-3-iodopropane}}{CH_2Br \cdot CHBr \cdot CH_2I} \ ;$$

$$CH_2 = CH - CH_2I + HBr \longrightarrow \underset{2-\text{Bromo-1-iodopropane}}{CH_3CHBrCH_2I}$$

Allyl iodide is widely used in organic synthesis.