

# Haloalkanes and Haloarenes

# HALOALKANES (ALKYL HALIDES)

- Compounds in which one or more hydrogen of alkane is (are) replaced by halogen are known as **haloalkanes**.
- Halogen derivatives can be categorized into two types depending upon the nature of hydrocarbons as :
  - Halogen derivatives of saturated hydrocarbon

e.g. 
$$C_n H_{2n+1} \lambda$$

Halogen derivatives of unsaturated hydrocarbons e.g. C Hand X and C Hand X

$$CH_{4} \xrightarrow{+X}_{-H} CH_{3} \xrightarrow{-X} \xrightarrow{+X}_{-H} CH_{2} \xrightarrow{X}_{-H} \xrightarrow{+X}_{-H}$$
Methane
$$H \xrightarrow{-X}_{X} \xrightarrow{+X}_{-H} CH_{2} \xrightarrow{X}_{-H} \xrightarrow{+X}_{-H}$$

$$H \xrightarrow{-X}_{X} \xrightarrow{+X}_{-H} X \xrightarrow{-X}_{X} \xrightarrow{-X}_{-H} \xrightarrow{-X}_{X}$$
Trihalo
methane
$$Tetrahalo$$
methane
$$Tetrahalo$$
methane

#### Nomenclature

• According to common or trivial system, monohaloderivatives are named as alkyl halides.

For example;

 $CH_3 - CI$  (methyl chloride)

 $CH_3 - CH_2 - I$  (ethyl iodide)

 According to IUPAC system, the monohaloderivatives of alkanes are named as haloalkanes.

CH<sub>3</sub> — CH — CH<sub>3</sub> (2-bromopropane) I Br

$$CH_3 - CH - CH_2 - Br (1 - bromo-2 - methylpropane)$$

• If different halogen atoms are present in a chain then we write them alphabetically and also counting will be done from that side by which halogen (bromine) gets the least possible position followed by chlorine, fluorine and iodine alphabetically.

$$\overset{1}{CH}_{3} - \overset{2}{\overset{CH}{\underset{|}{\overset{|}{Br}}} } \overset{3}{\overset{CH}{\underset{|}{\overset{-}{CH}}} - \overset{4}{\overset{CH}{\underset{|}{CH}}} \overset{4}{\underset{|}{Cl}} (2\text{-bromo-4-chlorobutane})$$

## Preparation

$$\frac{\text{PCl}_{5}}{|\text{HCl}, \text{ZnCl}_{2}|} \approx RCl + \text{POCl}_{3} + \text{HCl}$$

$$R-OH = \underbrace{\frac{SOCl_2}{Pt+I_2}} RCl + SO_2 + HCl$$

$$RI + H_3PO_3$$

•  $R - H + X_2 \xrightarrow{h \upsilon} RX + HX$ 

$$R - Cl + NaI - \frac{Acetone}{RI} + NaCl$$

• Hunsdiecker reaction :  $RCOOAg + Br_2 \xrightarrow{CCl_4} RBr + CO_2 + AgBr$ 

## Nature of C — X Bond

- In haloalkanes, the halogen atom is bonded to an alkyl group. The carbon atom is  $sp^3$  hybridised.
  - They are further classified as primary (1°), secondary (2°) and tertiary (3°) halides depending upon whether the halogen atom is attached to a primary, secondary or tertiary carbon atom.
  - The C X bond is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms. Halogen tends to pull the electrons away from carbon due to high electronegativity.

This positive charge on carbon makes it susceptible for nucleophilic attack.

 In haloalkanes bond strength of C – X bond decreases with an increase in bond length as one moves from fluorine to iodine.

$$C - F \xrightarrow{C - Cl} C - Br \xrightarrow{C - I}$$

#### **Physical Properties**

- Alkyl halides being polar in nature are water insoluble as they cannot break H-bonding already existing in water.
- Greater the molecular mass, stronger the van der Waals' forces of attraction and hence higher are the melting and boiling point. For the same alkyl group boiling point follows the order as :

R - I > R - Br > R - Cl > R - F

- As on increasing branching, surface area is decreased hence van der Waals' forces of attraction is decreased and hence boiling point is decreased.
- Decreasing order of density among the alkyl halides will be RI > RBr > RCl > RF.
- Stability order of R X is as follows : R - F > R - Cl > R - Br > R - I.
- It is alkyl iodide which decomposes in the presence of sunlight. Thus alkyl iodide on standing becomes violet or brown.

$$2RI \xrightarrow{\text{Sunlight}} R - R + I_2$$

• The I<sub>2</sub> thus liberated dissolves in alkyl iodide to impart it a dark colour.

#### **Chemical Properties**

- Mechanism of substitution reactions : Due to the presence of C X bond, alkyl halides are highly reactive compounds. They are known to undergo nucleophilic substitution reactions. Nucleophilic substitution reactions are of two types :
  - S<sub>N</sub>1 (Nucleophilic substitution unimolecular)
  - $S_N^2$  (Nucleophilic substitution bimolecular)
  - >  $S_N 1$  reaction : As name indicates, it is a first order reaction *i.e.* rate of reaction depends upon the concentration of substrate only, not upon the concentration of nucleophile. This reaction occurs in two steps. In the first step there is heterolytic cleavage of C — X bond to generate a carbonium ion which is a planar species *i.e.* carbonium ion carbon is in  $sp^2$ hybridized state. Since it is a slow step, hence it is rate determining step too.

In second step nucleophile attacks on carbocation to give the substituted product immediately as carbocation is highly reactive species. This step is fast step hence it does not affect the rate of reaction.

During  $S_N^1$  reaction optically active reactant will give optically inactive product *i.e.*, racemic mixture is obtained. All the tertiary alkyl halides undergo  $S_N^1$  reaction.

>  $S_N^2$  reaction : As name indicates, it is a second order reaction. *i.e.*, rate of reaction depends upon the concentration of alkyl halide as well as nucleophile. During the  $S_N^2$  reaction no carbocation is formed but transition state is achieved as it is a simultaneous process. Since the nucleophile attacks from the back side, hence we get product having configuration opposite to the reactant *i.e.*, inversion of configuration takes place in  $S_N^2$  reaction which is also said to be Walden inversion.



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- **Chemical reactions :** Because of the polar nature of R X bond, alkyl halides are highly reactive compounds. They undergo nucleophilic substitution reactions and elimination reactions.
  - Nucleophilic substitution reactions : Alkyl halides easily undergo nucleophilic substitution reactions. Weakly basic halide ion is a good leaving group and gets replaced by other nucleophile easily.

Elimination reactions-Dehydrohalogenation : Alkyl halides undergo -elimination reaction in the presence of potassium hydroxide in ethanol to yield alkene, by E1 or E2 mechanism according to the structure of alkyl halides.

$$CH_2 - CH - CH_3 \xrightarrow{K \oplus H (alc.)} CH_3 - CH = CH_2 + HBr$$

$$|$$
Br

In case of unsymmetrical alkyl halides, the course of elimination is determined by **Saytzeff's rule** according to which hydrogen is eliminated preferentially from the carbon atom which has less number of hydrogen atoms and thus highly substituted alkene is the major product. For example,

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} - C$$

Order of reactivity of alkyl halides towards dehydrohalogenation is (both El and E2)  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

Reduction : Alkyl halides can be reduced by Zn—Cu couple and alcohol or zinc and hydrochloric acid or lithium aluminium hydride to give alkanes.

$$CH_{3}CH_{2}Cl \xrightarrow[or Zn/HCl or LiAIH_{4}]{} CH_{3}CH_{3} + HCl$$

Alkyl iodides can be reduced with HI and red phosphorus.

$$CH_3CH_2 - I + HI \xrightarrow{\text{Red }P} CH_3 - CH_3 + I_2$$

- > Reaction with metals :
  - With Magnesium : Alkyl halides on reaction with magnesium in ether solution form alkyl magnesium halides (*RMgX*) commonly known as Grignard Reagent (Named after Victor Grignard).

 $CH_3I + Mg \xrightarrow{Ether} CH_3MgI$ Methyl magnesium iodide

 Reaction with sodium (Wurtz Reaction) : Alkyl halides on reaction with sodium in presence of dry ether form alkanes. The reaction is commonly known as Wurtz reaction.

R - X + 2Na + X - R Dry ether R - R + 2NaX

 Reaction with lithium : Alkyl halides form lithium alkyls on reaction with lithium. These are more reactive than Grignard reagents.

$$CH_3 - CH - CH_3 + 2Li \xrightarrow{- \to} CH_3 - CH_3 - CH_3 + LiBr$$
  
Br Li

 Wurtz-Fittig reaction : Alkyl halides on reaction with aryl halides and sodium in presence of dry ether give substituted benzene.



- **Correy-House reaction :** Alkyl halides on reaction with copper dialkyl lithium  $(R_2CuLi)$  form alkanes.

$$RX \xrightarrow{\text{Li/Et_2O}} RLi \xrightarrow{\text{CuI}} R_2\text{CuLi}$$

 $R'X + R_2$ CuLi  $\longrightarrow R' - R + R$ Cu + LiX

#### **Optical Rotation**

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- Substances which rotate the path of plane polarised light to either left or right are known as optically active and the rotation is known as **optical rotation**.
- If the substance rotates the plane polarised light in clockwise direction (*i.e.*, to the right) it is called **dextrorotatory or d form** and if the substance rotate the plane polarized light in anticlockwise direction (*i.e.*, to the left), it is called **laevorotatory or l form**.
- The optical rotation of an optically active compound is expressed in terms of specific rotation.

specific rotation =  $\frac{Observed rotation in degrees}{length(dm) \times conc.(g/mL)}$ 

- The compounds which differ only in the behaviour towards polarised light are called optical isomers and the phenomenon is called **optical isomerism**.
- Alkyl halides show optical isomerism. Basic requirement for the presence of optical isomerism is
  - Compounds must have a chiral or asymmetric carbon atom *i.e.*, a carbon atom should be linked to four different groups.
  - Mirror images must be non-superimposable (non superimposable mirror images are said to be enantiomers).
- Lowest molecular mass, optically active haloalkane must contain four carbon atom.



In the given structure there is presence of one chiral carbon atom which is linked to four different groups. These are

$$\begin{array}{c} - \mathrm{H}, - \mathrm{X}, - \mathrm{CH}_{3} \text{ and } - \mathrm{CH}_{2} - \mathrm{CH}_{3}. \\ & \mathsf{CH}_{3} \\ & \mathsf{H} - \mathsf{C} - \mathsf{C} \mathsf{I} \\ & \mathsf{H} - \mathsf{C} - \mathsf{C} \mathsf{I} \\ & \mathsf{I} \\ & \mathsf{C}_{2} \mathsf{H}_{5} \\ & \mathsf{C} \mathsf{I} \\ & \mathsf{C}_{2} \mathsf{H}_{5} \end{array} \begin{bmatrix} \mathsf{C} \mathsf{H}_{3} \\ & \mathsf{C} \mathsf{H}_{3} \\ & \mathsf{C} \mathsf{I} \\ & \mathsf{C} \mathsf{I} \\ & \mathsf{C}_{2} \mathsf{H}_{5} \\ & \mathsf{C} \mathsf{I} \\ & \mathsf{I} \\ & \mathsf{C} \\ & \mathsf{C} \\ & \mathsf{C} \\ & \mathsf{C} \\$$

A and B are mirror images of each other or enantiomers (enantiomers have same physical and chemical properties). Also they rotate the plane of polarized light upto the same extent, but in opposite directions.

### HALOARENES (ARYL HALIDES)

#### Nature of C — X Bond

In haloarenes, the carbon atom attached to halogen is sp<sup>2</sup> hybridized. The sp<sup>2</sup> hybridized carbon atom with a greater s-character is more electronegative thus, the sp<sup>2</sup> hybridized carbon holds the electron pair more tightly than the sp<sup>3</sup> hydridized carbon of haloalkanes. Therefore, the C --- X bond in haloarenes is shorter than in haloalkanes.