

Halo Alkanes and Haloarenes

Alkyl Halides

Synopsis

- * Halogen derivatives of hydrocarbons either aliphatic or aromatic are known as halogen compounds. (Alkyl halide or haloalkane; aryl halide or haloarenes)

Classification of Halogen compounds

- * On the basis of number of halogen atoms, haloalkanes and haloarenes may be classified as mono, di, or poly (tri, tetra.....etc) halo compounds.

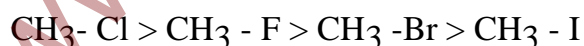
Allylic halides :- These are the compounds in which the halogen atom is bonded to an sp^3 - hybridised carbon atom next to carbon-carbon double bond (C=C) i.e. to an allylic carbon.

- * Benzylic halides are again classified into 1^0 , 2^0 , 3^0 -benzylic halides
- * If R^1 , R^{11} are hydrogens, it is 1^0 -benzylic halide
- * If R^1 is an alkyl group, R^{11} is hydrogen then it is 2^0 -benzylic halide
- * If R^1 and R^{11} are alkyl groups, then it is 3^0 -benzylic halide.

Aryl halides : - These are the compounds in which the halogen atom is bonded to the sp^2 - hybridised carbon atom of an aromatic ring.

- * Dihaloalkanes having same halogen atoms on the same carbon atom are called geminal halides (or) alkylidene halide.

Dipole moment Order



- * i) Dipole moment decreases as the electronegativity of the halogen decreases from Cl to Br to I. Fluorides, however, have lower dipole moment than chlorides.
- * Alkyl halides are colourless but bromides and iodides get colour on exposure to light.
- * They have pleasant odour.

- * Lower alkyl halides are gases but higher alkyl halides are liquids and solids.
- * Alkyl halides are more polar and with more molecular masses when compared with parent hydrocarbons. Because of these reasons they have stronger inter molecular forces of attraction and possess high b. pts and m. pts compared to parent hydrocarbons.

Melting and boiling points. Greater the molecular mass, stronger the Van der Waals forces of attraction and hence higher is the melting point/boiling point.

- For the same alkyl or aryl group boiling points decrease as: $RI > RBr > RCl > RF$.
 - For the same halogen, boiling points decrease as the size of the alkyl group decreases: $CH_3CH_2CH_2X > CH_3CH_2X > CH_3X$ where $X = F, Cl, Br, I$.
- * Haloalkanes are very slightly soluble in water but highly soluble in organic solvents like CCl_4 . (like dissolves like)
 - * Colourless gas (B.P. $13^\circ C$ or $286K$) with pleasant odour. Its density is 0.91 gm/ml .
 - * It is soluble in organic solvents like CCl_4 , ether but almost insoluble in water.
 - * It does not form a precipitate with $AgNO_3$ solution; because C-Cl bond is covalent. It does not give Cl^- ions in solution.
 - * The precautions to be taken in storing chloroform are
 - 1) It is stored in stoppered dark-blue or brown coloured bottles to prevent the entry of light
 - 2) It is filled up to the brim to avoid exposure to air
 - 3) About 1% Ethyl alcohol is added as a preservative
 - * The impurity usually present in chloroform is phosgene (or) carbonyl chloride ($COCl_2$)
 - * The reagent used for testing the purity of chloroform is **$AgNO_3$** .

- * With impure chloroform, AgNO_3 gives a white precipitate of AgCl . Here the species which gives white ppt is HCl . (produced by the oxidation of chloroform.)
- * It is prepared in the laboratory or industrially by heating ethyl alcohol or Acetaldehyde or Acetone with bleaching powder and water. (Or with chlorine and alkali)

Mechanism of Substitutions reactions (SN^1 & SN^2)

- * Carbon compounds in which a sp^3 carbon is bonded to a relatively more electronegative atom or group undergo mainly two types of reactions.
- * Substitution reactions follow two types of mechanism. These are
 - 1) SN^1 reaction
 - 2) SN^2 reaction
- * Irrespective of the mechanism by which the substitution reaction occurs, it is called nucleophilic substitution reaction because a nucleophile is substituted for the halogen. The mechanism depends on
 - i) The structure of alkyl halide
 - ii) The reactivity and structure of nucleophile
 - iii) The concentration of the nucleophile and
- * All tertiary alkyl halides undergo substitution reactions by SN^1 mechanism.
- * SN^1 mechanism is facilitated by polar protic solvents, such as water, alcohol or aqueous-organic solvents. Such solvents promote the ionisation step by stabilizing the ions by solvation.
- * Primary allylic and primary benzylic halides show higher reactivity in SN^1 reactions than other primary alkyl halides. This is due to greater stabilisation of the allylic and benzylic carbocations intermediates by resonance.

SN^2 (substitution, Nucleophilic, Bimolecular) Mechanism: The rate of SN^2 reaction depends upon the concentration of both the alkyl halide as well as the nucleophile. This implies that both the reactants are taking part simultaneously in the

rate determining step of the reaction. In other words, S_N2 reactions are concerted reactions, i.e. they occur in one step. Such reactions occur through a transition state in which both the reactant molecules are partially bonded to form a transition state which later dissociate into products.

- * S_N2 reactions are always accompanied by inversion of configuration, which is known as Walden inversion.
- * If the alkyl halide is optically active, the product is also optically active.
- * Primary alkyl halides almost always react predominantly by S_N2 mechanism whereas tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides react by either mechanism, depending on the nature of the nucleophile and the solvent.
- * Whether the reaction is going to be substitution or elimination, it depends on several factors like nature of alkyl halide, strength and size of nucleophile, the reaction condition etc.
- * A bulky nucleophile prefers elimination reaction; a primary alkyl halide prefers S_N2 reaction, a tertiary alkyl halide S_N1 or elimination depending on the stability of carbocation or product alkene and a secondary alkyl halide for S_N2 or elimination depending on nucleophile.
- * Halo arenes are obtained by the replacement of hydrogen atom of (an arene) aromatic hydrocarbon by halogen.
- * Halo arenes are named by adding the prefix halo before the name of the aromatic hydrocarbon. In case of disubstituted compounds, the relative position of the substituents 1, 2 or 1, 3 or 1, 4 are indicated by the prefixes ortho, meta and para respectively.
- * In aryl halides, C-X bond gets partially double bond character due to resonance. As a result, C-X bond is stronger in aryl halides than in alkyl halides. C-Cl bond length is 177pm in halo alkane (ethyl chloride) but 169pm in Chlorobenzene.

- * Iodobenzene cannot be prepared by the above method as the reaction is reversible, HI formed should be immediately oxidised using oxidising agents like HNO_3 , HIO_4 etc.
- * F_2 being reactive, fluorides are not prepared by this method.

Nucleophilic substitution reactions: Aryl halides are extremely less reactive towards $\text{S}_{\text{N}}1$ reaction than haloalkanes.

- * Dichloromethane is widely used
 - i) As a solvent as a paint remover
 - ii) As a propellant in aerosols
 - iii) As a process solvent in the manufacture of drugs, propellant in aerosols.
 - iv) As a metal cleaning and finishing solvent.

HaloAlkanes: Haloalkanes and haloarenes are obtained by the replacement of a hydrogen atom of an alkane and arene respectively by a halogen atom (F, Cl, Br and I).

Their general formulae are

Halo alkane: RX "R" is alkyl group.

Halo arene: ArX where 'Ar' is arene.

- * Order of reactivity of hydrogens



- * Direct iodination is not possible as the reaction is reversible. Iodination is carried by using oxidising agents like HNO_3 or iodic acid.
- * The reactivity of different types of hydrogen's in this free radical halogenation is benzylic > Allylic > tertiary > secondary > primary > vinylic aryl. This order is opposite to the C-H homolytic bond dissociation energies.
- * Since the vinylic and aryl hydrogen's are more unreactive, vinyl halides and aryl halides can not be prepared by free radical halogenation.

- * Alkyl bromide can be prepared by heating C_2H_5OH with HBr and conc. H_2SO_4 . But this method is not used in the case of secondary and tertiary alcohols as their dehydration may occur.
- * Alkyl iodides are prepared by refluxing alcohol with excess of HI (or) by heating with KI in the presence of H_3PO_4 .
- * CH_3F , CH_3Cl , CH_3Br and C_2H_5Cl are gases at room temperature.
- * Other alkyl halides up to C_{18} are colorless liquids.
- * Alkyl halides burn with a green edged flame.
- * Alkyl halides are generally toxic and can cause unconsciousness.
- * **Bond strength** decreases as the size of the halogen increases: $CH_3F > CH_3Cl > CH_3Br > CH_3I$.