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HALOAREANS AND HALOALKANES

HALOARENES & HALOALKENES

The halogen derivatives of aliphatic & aromatic hydrocarbons are called halo alkenes & haloarenes. White hydroxy alcohols & phenols resp.

Haloalkanes & haloarenes are obtained by the replacement of a hydrogen atom of an alkane & arene resp by a halogen atom (F, Cl, Br, & I)

The general formula are Haloalkane: RX where R is alkyl group

Haloarene: ArX where Ar is arene X is a halogen atom (F, Cl, Br, I)

HALOALKANES

The haloakanes are monohalogen derivatives of alkanes these are also called alkyl halides these are formed by replacing one hydrogen atom in alkane by a halogen.

-H R-H → R-X haloalkane or alkyl halide

Ex CH4 $\xrightarrow{-H}$ CH₃Cl

(Chloromethane or methyl chloride)

The general formula of haloalkane or alkyl halide is $C_n H_{2n+1} X$ (or RX) Where R- alkyl group

X- Halogen atom

Polyhalogen derivatives of alkanes or polyhaloalkanes

The compounds in which more than one hydrogen atoms of the alkane molecule have been replaced by halogen atoms. The prefixes n, iso, neo are used for the fall alkyl groups

n CH₃CH₂CH₂CH₂ or the n is used for alkyl group having continuous chain of C atoms with branching



the prefix iso is used for those alkyl group in

which one methyl group is attached to next to end $\ensuremath{\mathsf{c}}\xspace$ atom

neo
$$CH_3$$
 CH_3
 I I I
 H_3 $C-CH_2$ or $CH_3-C-CH_2-CH_2$
 I I
 CH_3 CH_3

the prefix neo is used for those alkyl group in which have two methyl group attached to the next to end C-atom

DIHYDROGEN ALKANES

Alkylidence dihalides or alkylidene halides when both the halogen atoms are attached gem dihalides.

To the same C- atom, these are called gem dihalides.

Ex CH₃CHCl₂

Ethylidene dichloride

³ CH₂Br iso propylidene dichloride IUPAC-2-2-Dichloropropane

two Cl atoms on same C atom

Alkylene dihalide or alkylene halide or vicinal Dihalides.

When the two-halogen atoms are in adjacent C atoms, they are called vicinal dihalides.

Ethylene dichloride IUPAC-1-2-dichloro ethene

$$CH_3$$

 H_3
 CH_3 -C-CH₂Br
 H_3 iso buty
Br HUDAC

r iso butylene dibeomide IUPAC-1-2-dibeome-2-methyl propane

CLASSIFICATION OF ALKYL HALIDES

Alkyl halides or haloalkanes are classified as primary (1°) secondary (2°) or tectiry (3°) depending upon the nature of carbon ato to which the halogen is attached

(I) **Primary haloakanes are** those which have one or more alkyl group on the carbon linked to the halogen atom.

(II) Secondary haloalkanes are those which have two alkyl groups on the carbon linked to the halogen atom.



Aralykyl halides : These are the compounds in which the hydrogen atom of a side chain (mainly an alkyl group) is replaced by a halogen atom. **Note :** C.H.X CH. CH.X

 C_2H_5X CH_2 CH_2X Mono halo alkane CH_2X CHX

> Dihaloalkane CH₂X Trihaloalkane

Chemical properties of haloalkanes

The reaction of haloalkanes may be divided into the following categories

- 1) Nucleophilie substitution reaction
- 2) Elimination reaction
- 3) Reaction with metals
- 4) Reduction

Nucleophilie substitution reaction

In haloalkanes the carbon is bonded to a halogen atom which more electronegative than carbon . The C-X bond is polae in nature . carbon gets partial positive charge(8)+ and the halogen atopm gets partial negative charge (8)- . The presence of partial positive charge on the carbon atom made it susceptible to attack by electron rich group called nucleophiles . When a nucleophile stronger than a halide ion approaches the positively charged. Carbon atom of an alkyl halide , the halogen atom along with its bending electron pair gets displaced and a new bond with the carbon and the nucleophile is bformed . These reactions are nucleophile S.R.

C X + :Nu C NU + :X Nucleophile halide ion

Ex. $CH_3CH_2Br + OH^2$

 $CH_3CH_2OH + : Br^{-1}$

The atom or group of atoms which loses its bond to carbon and takes on an additional pair of electron is called leaving group halide ions are good leaving group.

Note : Better the leaving group , the faster is the N.S.R. iodide ion is best L.G. therefore iodoalkanes undergo N.S.R. at faster rate. Frolide ion is poorest leaving group.

Reaction of haloalkanes

1) Substitution by hydroxyl group (formation of alcohols) :-

Haloalkanes react with boiling ap alkali (KOH) or Ago2 to form alcohols

RX +	KOH⁻	\rightarrow	ROH + KX		
Haloalkane			alcohol		

 $\begin{array}{rcl} \textbf{Ex.} \ \textbf{CH}_{3}\textbf{CH}_{2}\textbf{Be} \ + \ \textbf{KOH} \ \rightarrow \ \textbf{CH}_{3}\textbf{CH}_{2}\textbf{OH} \ \ + \ \ \textbf{KBr} \\ & \text{ethanol} \end{array}$

2). Substitution by alkoxl group (formation of ether) When ethyl is treated with Na or potassium alkoxides , ether is formed .

RX	+	Na+OR	\rightarrow	R - O - R	+	NaX
Sod.alkoxide			ether			

 $\begin{array}{rcl} \mathsf{CH}_3\mathsf{CH}_2\mathsf{Br} \ + \ \mathsf{Na} + \mathsf{OC}_2\mathsf{H5} & \to \mathsf{CH}_3\mathsf{CH}_2\mathsf{OC}_2\mathsf{H}_5 \ + \ \mathsf{Na}\mathsf{Br} \\ & & \mathsf{Sodium} & \mathsf{ethox}\mathsf{I} \ \mathsf{ethane} \\ & & \mathsf{Ethox}\mathsf{ide} & (\mathsf{diethyl} \ \mathsf{ether}) \end{array}$

The N.S.R. of alkyl halides proceed in the following two type of mechanisms.

1). Substitution nucleophilic bimolecular S_{N}^{2}

2). Substitution nucleophilic unimolecular \hat{S}_{N}^{1}

S.N.B. S_N² reaction

The reaction between methyl bromide (CH₃Br) and hydroxide ion (OH) to from methanol follow a second order (ii) Depends upon the concentration of both reactions (alkyl halide & hydroxide ion)

CH₃Br + OH⁻ → CH₃OH + Br⁻ Alkyl halide hydroxide methyl Or Nucleophile

Rate=k [CH₃Br] [OH⁻]

Primary or methyl halides follow this type of mechanism it can be written as:-

Rate = k [RX] [OH-]

This reaction is called N.S.B.R become 2-molecule take part in determining the rate of the reaction. This reaction occurs in one-step through the formation of transition state. The incoming nucleophile interacts with alkyl halide causing the carbon halide bond to break while forming a new carbon -OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. The bond between the nucleophile and the carbon atom starts forming the bond attack inverts in much the same way as on umbrella is trained inside out when caught in a strong wind, while the leaving group is pushed away. This process is called as inversion of configuration or healden inversion, in case of optically active alkyl halide, the product obtained has an inversion of configuration (ii) there is change in sign of rotation from (+) to (-) and versa for example (-)-2bromobutane on treatment with aq KOH solution gives (+)-2-butanol as the product

HO-
$$\longrightarrow$$
 C -- Br $\xrightarrow{aq \text{ KOH}}$
HO-C + Br-
H₃CH₂C
(-)-2-bromobutane

Thus SN_2 reaction of optically active alkyl halide are accompanied by inversion of configuration.

CH3

CH

1º-alkyl halide

The transition state is unstable because carbon atom is bonded to 5 atoms and changes to products in which bromide ion forming a C-OH bond. The formation of transition state is ratedetermining step and the rate of reaction depends upon concentration of both alkyl halide and OH-. Hence, it is an II^{nd} order reaction or bimolecular reaction.

Reason; - or sterei effect in SN2 reaction

The reactively of alkyl halide towards $S_N^{2,r}$ mechanism is in the following order:-

Methyl halide >primary halide > secondary halide > tert halide

Ans the presence of bulky substituents on or near the carbon hinders the attract of nucleophile and slow the reaction. This interference of the bulky groups with a reaction is called **stearic hindrance** in simple alkyl halide or methyl halides react most rapidly in S_N^2 reaction because there are only there small hydrogen atoms (react satearic hindrance) tert alkyl halides are least reactive because of the presence of 3 bulky groups on carbon (maximum staeric hindrance).

The order of reactively is;-

 $CH_X > 10 > 2^\circ > 3^\circ alkyl halide.$

Substitution N, unimolecule S_N¹reactions;-

The reaction between tert-butyl bromide and hydroxide ion to form tert butyl alcohol. Follows 1^{st} order (ii) the rate depends on the concentration of one reactant only i.e. alkyl halide.

The rate reaction

Rate = $k [(CH_3)_3(Br)]$

Or rate = k [RX]

Such type of reactions are carried in polar solvents as water, alcohol, ascertained this is called S.N unimolecular because only one molecule is involved in determining the rate of the reaction.

SN¹ mechanism occurs in 2 steps

Step I the polarized C-halogen bond (C-Br) undergoes slow develop to form a carbocation and bromide ion.

Step II the carbocation is very reactive species. It readily reacts with a nucleophile, OH- to form the product.

The Ist step is slow and reversible. It involves the of C-Br bond for which energy is obtained through salvation of bromide halide ion with the proton of the Solvent. The slowest step is the rate-determining step. The rate of reaction depends only on the ... of tert-butyl bromide (alkyl halide) it is a Ist order of unimolecular reactions.

Reactively of alkyl halides towards S_N^{1} **reaction** The order of reactively depends upon the stability of carbocation in the Ist step. Greater the stability of the carbocation, greater will the rate of formation form alkyl halide and hence faster will be the rate of reaction. 30 carbocation is most stable. Tert alkyl halide>sec alkyl halide> primary A H > methyl halide

S Aspects of SN¹reactions

In case of O. active alkyl halide, the product obtained is a Mixture because the intermediate carbocation is planar species. The attack of nucleophile OH- can take place with equal case from both the faces (front and rear) 50;50 mixture of 2 which is optically inactive.

Elimination reactions (dehydrogenation).

When haloalkanes with .. Hydrogen atoms are boiled with alcoholic solution of KOH. They undergo elimination of HX (hydrogen halide) and form alkenes.

These reaction are called .. elimination reaction because the hydrogen atom present at .. position of haloalkane (i.e. at the carbon atom next to that which carries the halogen) is removed.

MECHANISM

The elimination reaction occurs by abstraction of proton from a carbon atom next to the carbon bearing halogen atom (called .. hydrogen) and a halide ion is also lost reselling a new bond.

Reaction with active metals

Active metals like Na, Mg, Cd, Li, combine with alkyl chlorides, bromides and iodides to give comp.

SOLVED PROBLEMS

Q.1 Name the following halides according to IUPAC system and classify them as alkyl, alkyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides. (i) (CH_3) , $CHCH(CI)CH_3$ (ii) CH,CH,CH(CH,)CH(C,H₂)Cl (iii) CH₃CH₂C(CH₃)₂CH₂I (iv) (CH₃)₃CCH₂CH(Br)C₆H₅ (v) CH₃CH(CH₃)CH(Br)CH₃ (vi) $CH_3C(C_2H_5)_2 CH_2Br$ (vii) CH₃C(Cl)(C,H₅)CH₂CH₃ (viii) CH₃CH=C(CI)CH₂CH(CH₃)₂ (ix) CH₃CH=CHC(Br)(CH₃)₂ (x) $P-CIC_6H_4CH_2CH(CH_3)_2$ (xi) $m-CICH_2C_6H_4CH_2C(CH_3)_2$ (xii) o-Br-C_eH₄CH(CH₅)CH₅CH₅ Ans. (i) 2-Chloro-3-methylbutane, 2° alkyl halide, (ii) 3-Chloro-4-methylhexane, 2° alkyl halide (iii) 1-Iodo-2,2-dimethylbutane, 1° alkyl halide (iv) 1-Bromo-3,3-dimethyl-1-phynylbutane, 2° benzylic halide (v) 2-Bromo-2-ethyl-2-methylbutane, 2° alkyl Q.3 halide (vi) 1-Bromo-2-ethyl-2-methylbutane, 1° alkyl halide (vii) 3-Chloro-5-methylpentane, 3° alkyl halide Ans. (i) (viii) 3-Chloro-5-methyhex-2-ene, vinylic halide (ix) 4-Bromo-4-methylpent-2-ene, allylic halide (x) 1-Chloro-4-(2-methylpropyl) benzene, aryl halide (xi) 1-Chloromethyl-3-(2, 2-dimethylpropy) benzene, 1° benzylic halide (xii) 1-Bromo-2-(1-methylpropyl) benzene, aryl halide. Q.2 Hydrocarbon C₅H₁₀ does not react with chlorine but gives a single monochloro compound, C_sH_aCl in bright sunlight. Identify the hydrocarbon. (i) The hydrocarbon with M.F. C_5H_{10} can be Ans. either a cycloalkane or an alkene.

(ii) Since the hydrocarbon does ot react with Cl_2 in the dark, in cannot be an alkene but must be a cycloalkane.

(iii) As the cycloalkane reacts with Cl_2 in the presence of bright sunlight, to give a single monochloro compound, C_5H_9Cl , therefore all the ten hydrogen atoms of the cycloalkane must be equivalent. Therefore, the cycloalkane is cyclopentane.



Write the equations for the preparation of 1-bromobutane from (i) I-butanol (ii) 1chlorobutane (iii) but-1-ene.

ns. (i) $3CH_3CH_2CH_2CH_2OH+PBr_3 \xrightarrow{\text{from } (P\&Br_2)}$

1-Butanol

 $3CH_3CH_2CH_2CH_2Br + H_3PO_3$ 1-Bromobutane

(ii) $CH_3CH_2CH_2CH_2CI+NaBr \xrightarrow{from (P&Br_2)}_{(Finkeltein reaction)}$

1-Chlorobutane

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CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br+NaCl
1-Bromobutane
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(iii) CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}_{\text{Anti-Mark, addn.}}
But-I-ene CH_3CH_2CH_2CH_2Br
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1-Bromobutane

Q.4What are ambident nucleophiles ? Explain
with an example.Q.6Arrange the compounds of each set in order
of reactivity towards S₄2 displacement :
(i) 2-Bromo-2-methylbutane,
1-Bromopentane, 2-Bromopentane.Ans.The nucleophiles which can attack through two
different sites are called ambident nucleophiles.
For example, cyanide ion is a resonance hybrid
of the following two structures :
":CEN:
$$\rightarrow$$
 :C=N:"
T:CEN: \rightarrow :CeN:"
T:CEN: \rightarrow :CeN: \rightarrow :

HALOAREANS AND HALO ALKANES

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Due to steric reasons, the order of reactivity of alkyl halides in $S_N 2$ reactions follows the order. 1°>2°>3°, therefore, the order of reactivity of the given alkyl bromides is as follows :

1-Bromo-3-mythylbutane > 2-Bromo-3methylbutane > 2-Bromo-2-methylbutane.



As in case of 1° alkyl halides steric hindrance increases in the order : n-alkyl halides, alkyl halide with a substituent at any position other than the β -position, one substituent at the β -position, two substituents at the β -position, therefore the reactivity decreases in the same order. Hence, the reactivity of the given alkyl bromides decreases in the order :

1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2, 2-dimethylpropane.

Q.7 Out of C₆H₅CH₂Cl and C₆H₅CHClC₆H₅ which is more easily hydrolysed by aqueous KOH.

C₆H₅CH₂Cl is a 1° aralkyl halide while Ans. $C_6H_5CH(CI)C_6H_5$ is a 2° aralkyl halide. In S_N1 reactions.

> Ionization C_6H_5 $\rightarrow C_6H_5 - CH - C_6H_5 + CI^-$ ·CH-Carbocation stabilized by elocalisation over two C_sH_s rings CI 1-Chloro-1, 1-diphenylmethane Ionization

C₆H₅CH₂CI Benzyl chloride



reactivity depends upon the stability of carbocations, Since the carbocation $C_6H_5CHC_6H_5$ (where the +ve charge is delocalised over two C_6H_5 rings) derived from C_6H_5 – $CHClC_6H_5$ is more stable than the

carbocation, $C_6H_5CH_2$ (where +ve charge is

delocalised over one C_6H_5 ring) derived C₆H₅CH₂Cl, therefore, C₆H₅CHClC₆H₅ gets hydrolysed more easily than C₆H₅CH₂Cl under S_N1 conditoins.

Although, under S_{N2} conditions, the reactivity depends on steric hindrance, therefore, under $S_N 2$ conditions, $C_{e}H_{s}CH_{2}CI$ get hydrolysed more easily than C₆H₅CHClC₆H₅.

Why is chloroethane insoluble in water? Q.8

Ans. Chloroethane is unable to form hydrogen bonds with water. Hence, it is insoluble in water.

Q.9 Give one chemical test to distinguish between C,H,Br and C,H,Br.

- Ans. Hydrolysis of C₂H₅Br with refluxing aqueous KOH followed by acidification with dil. HNO₃ and subsequent treatment with AgNO₃ gives light yellow ppt. of AgBr whereas C₆H₅Br does not give this test.
- Q.10 Account for the following :

Haloalkanes undergo nucleophilic substitutions whereas haloarenes undergo electrophilic substitutions.

Ans. Haloalkanes are more polar than haloarenes. As a result the carbon atom carrying the halogen in haloalkanes is more electron-deficient than that in haloarenes. Consequently, haloalkanes undergo nucleophilic substitutions more readily than haloarenes.

> On the other hand, haloarenes contain a benzene ring. Since the typical reactions of benzene are electrophilic substitutions, therefore, haloarenes undergo electrophilic substitutions while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitutions.





