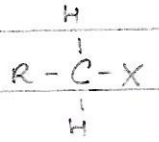
Halogenoalkanes

Q-1) What are halogenoalkanes?

> Halogenoalkanes are alkanes that have one or more hydrogen atoms replaced by a halogen.

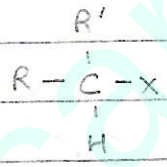
primary haloalkane (1° Rx).

- carbon with 1 alkyl group + 2 hydrogen groups.



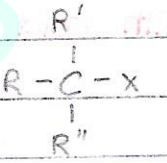
secondary haloalkane (2° Rx)

- carbon with 2 alkyl groups + 1 hydrogen atom.



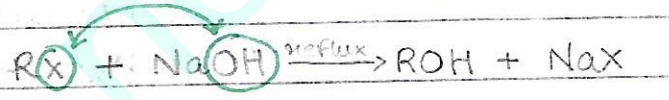
tertiary haloalkane (3° Rx)

- carbon with 3 alkyl groups + 0 hydrogen atoms.



Q-2) Nucleophilic substitution reactions of haloalkanes.

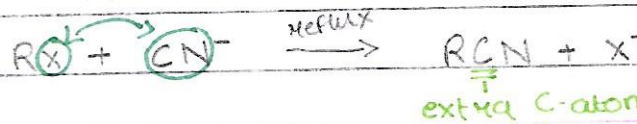
① Reaction with alkali NaOH / OH^- (aq). (or KOH)



eg: $CH_3CH_2Br + OH^- \xrightarrow{reflux} CH_3CH_2OH + Br^-$

A same reaction occurs with water, but slower because the negatively charged OH^- ion is a more effective nucleophile ~~that~~ than water.

② Reaction with cyanide ions (in ethanol) CN^- / KCN (or NaCN)



R-CN can be broken down...

Reduction.

$R\text{-}CN + [H] \longrightarrow R\text{-}CH_2NH_2$

Hydrolysis

acidic $R\text{-}CN + H^+ \xrightarrow{H_2O} R\text{-}COOH + NH_3$

alkaline $R\text{-}CN + OH^- \longrightarrow R\text{-}COO^- + NH_3$

$(NaOH)$ $(R\text{-}COONa)$

└ salt of alkali formed

③ Reaction with ammonia (in ethanol) NH_3.

$Rx + NH_3 \xrightarrow{\Delta \text{ pressure}} R\text{-}NH_2 + Hx$

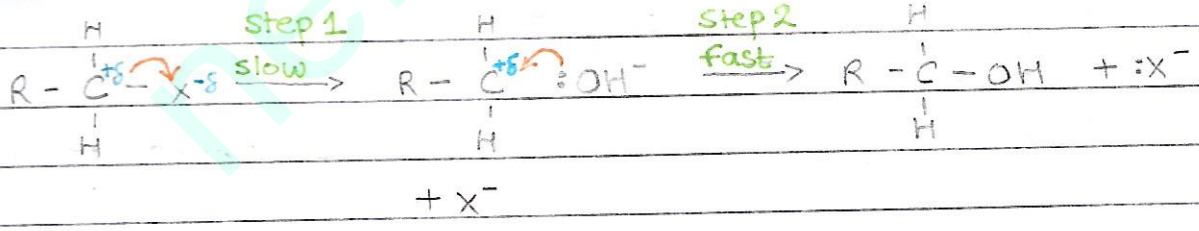
Q-3) Mechanism of nucleophilic substitution of halo-alkanes.

1° Rx = SN^2 mechanism

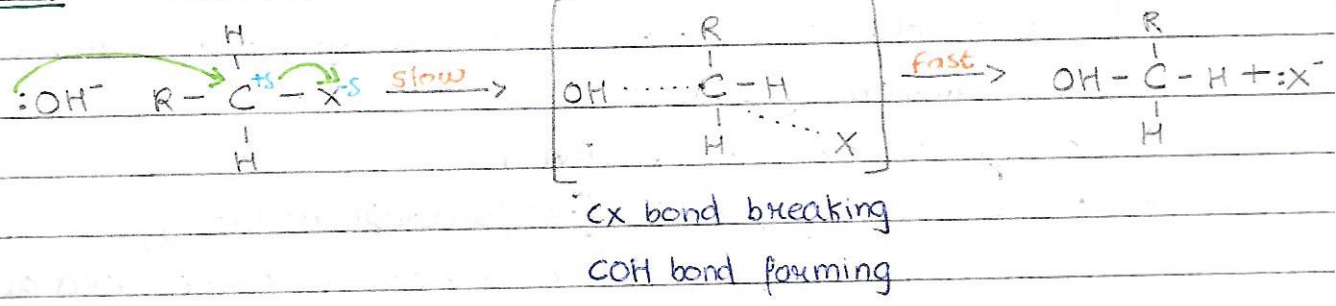
2° Rx =

3° Rx = SN^1 mechanism.

SN^1



SN^2



Cx bond breaking

COH bond forming

Q-4) Elimination reaction with alcoholic KOH / NaOH.

eg: $CH_3 - CH_2 - Br + KOH \longrightarrow CH_2 = CH_2 + KBr + H_2O$

H from the adjacent C-atom from X is removed.

Q-5) Stability of carbocations?

1° Rx - 1 methyl group transfers e⁻ (unstable)
∴ positive charge is not neutralised

2° Rx - 2 methyl groups transfer e⁻ (slightly unstable)
∴ positive charge slightly neutralised

3° Rx - 3 methyl groups transfer e⁻ (stable)
∴ positive charge neutralised.

↓

3° > 2° > 1° Rx

C-F
C-Cl
C-Br
C-I

Down the group atomic size ↑
∴ bond length ↑
∴ bonds are weaker
∴ less energy is required to break bonds.

Q-6) What are haloalkanes used for?

- anasthetics (haloethane)
- flame retardants (introducing a halogen into an alkane reduces its flammability)
- manufacturing plastics (PVC)
- non-stick lining of pans [poly(tetrafluoroethene)]
  strength of C-F bond means it can be used at high temperatures without breaking.