Halogenoalkanes

WHAT ARE THEY ?

- functional group = halogen atom.
- $C_nH_{2n+1}X$, X = F, Cl, Br, I
- nucleophilic substitution reaction
- no. of alkyl groups attached to C w/ halogen
  - ↳ primary, secondary, tertiary.
- 'fluoro', 'chloro', 'bromo', 'iodo'. (prefix)

PHYSICAL PROPERTIES

- Bp ↑ than alkanes of similar mass
  - ↳ C-X bond is polar ∴ has pd-pd
- Low solubility in H_2O
  - ↳ C-X bond not sufficient.

* compare vdw unless same Mr, then can compare pd-pd.

REACTIVITY

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

$\text{Reactivity} \xrightarrow[\text{decrease}]{}$

- atom size↑ ∴ bond weak, bond energy ↓, reactivity↑

ISOMERISM

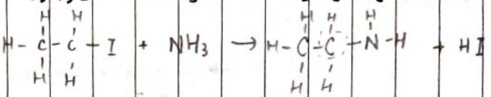
- structural

REACTIONS

Substitution	Elimination
→ KOH (aq) or H_2O (slower)	→ KOH conc. (alcoholic KOH)
→ heat	→ heat
→ OH^- ⇒ nucleophile	→ OH^- ⇒ base
→ OH^- subs. Br	→ H^+ removed
→ forms alcohol	→ forms alkene

SUBSTITUTION (H. ALKANE → AMINE)

$$C_2H_5I + NH_3 \longrightarrow C_2H_5NH_2 + HI$$



1° amine

→ conditions : EXCESS ammonia, alcoholic medium, heat in closed vessel under pressure.

SUBSTITUTION (H. ALKANE → NITRILE)

$$CH_3CH_2I + CN^- \longrightarrow CH_3CH_2CN + I^-$$

condition:

→ heat with ethanolic solution of NaCN / KCN

→ * increases carbon chain length.

or H. alkanes → amines
H-alkanes → nitriles

SUBSTITUTION (HALOGENOALKANES → ALCOHOL)

→ ✓ $CH_3CH_2Br \xrightarrow[\text{heat / heat under reflux}]{+\,KOH\,(aq)} CH_3CH_2OH + KBr$

the nucleophile:

$OH:^-$ (stronger)

∴ faster

Conditions : heat + KOH (aq)

OR

→ $CH_3CH_2Br + H_2O \xrightarrow[\text{heat}]{} CH_3CH_2OH + HBr$

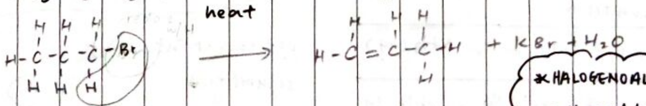
the nucleophile

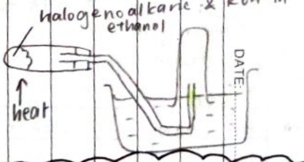
$H_2\ddot{O}:$

Conditions : heat + H_2O

ELIMINATION (HALOGENOALKANES → ALKENE)

→ $CH_3CH_2CH_2Br \xrightarrow[\text{heat}]{\text{conc. KOH (ethanol)}} CH_2{=}CHCH_3 + KBr + H_2O$





condition : heat + conc. alcoholic KOH

- OH^- acts as base, accepts proton to form H_2O (overall eliminates HBr)
- alcoholic medium so both can mix (KOH & halogenoalkanes)

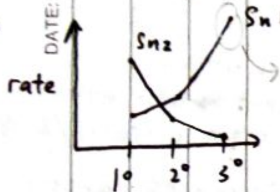
* HALOGENOALKANES to
→ ALCOHOL (KOH aq)
→ ALKENE (KOH ethanol)
→ AMINES (NH_3 ethanol)
→ NITRILES (NaCN / KCN ethanolic)

(all need heat)

Halogenoalkanes

REACTION MECHANISM

- → S_N1 (2 step, C–X break then nucleophile attack)
- → S_N2 (1 step, loss of X^- & gain of nucleophile simultaneous)
- → $S_N1 \Rightarrow 3°/2°$; $S_N2 \Rightarrow 1°/2°$
- →



→ 很 stable (3°), 所以 很 reactive

- → S_N2 faster w/ 1° H.alkanes than 3°
  - ↳ 3° H.alkanes, central carbon surrounded by bulky alkyl groups
  - ↳ transition state more crowded ∴ E_a ↑ so rate ↓

TEST FOR HALOGEN ATOMS IN H.ALKANES

- → warm w/ NaOH (aq) $\boxed{+ NaOH(aq) + HNO_3(aq)}$
- → add dilute HNO_3 (aq) to remove excess OH^-
- → add $AgNO_3$ and NH_3(aq) / NH_3 conc.
- → — C⫶X ⟶ $:X^-$ → can test w/ NH_3(aq)/ NH_3 conc.

heterolytic fission

$:OH^-$

→

HALOGEN	OBSERVATION
Cl (AgCl)	→ white ppt soluble in dilute NH_3
Br (AgBr)	→ cream ppt partially soluble in dilute NH_3 → cream ppt soluble in conc. NH_3
I (AgI)	→ yellow ppt insoluble in both dilute & conc NH_3

ppt colour intensity ↑
solubility ↓

ENVIRONMENTAL IMPACT

- → H.alkanes used in → herbicides
  - → pesticides
  - → polymers
  - → solvents
- → poly(chloroethene) (PVC) → packaging
- → poly(tetrafluoroethene) → "non-stick" surfaces
- → C–F bond very strong ∴ unreactive

CFC's

- → eg. dichlorofluoromethane $CHFCl_2$
  - trichlorofluoromethane CF_3Cl
- → used as → refrigerant
  - → aerosol propellant
  - → blowing agent
  - → fire extinguishers
- → chemically inert, non toxic, non flammable
- → CFC's break up in atmosphere to form free radicals $CF_2Cl_2 \rightarrow CF_2Cl\cdot + Cl\cdot$
- → catalyse breaking up of ozone. $2O_3 \rightarrow 3O_2$

replacements

- → can be replaced by HCFCs
  - ↳ more reactive
  - ↳ broken down @ lower altitude (avoid O_3 layer)
  - ↳ but greenhouse gas
- → or butane can replace, but flammable.
- → PVC can replace by polypropene.

PREPARATION OF H.ALKANES

From alkanes: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
↳ free radical substitution, UV

alkenes: $C_2H_4 + HBr \rightarrow C_2H_5Br$
↳ electrophilic addition, no conditions

alcohol: $C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$
↳ substitution reaction, acid catalyst (add at RT the heat under reflux)