Topic 10 – Haloalkanes
Revision Notes

1. General

- Functional group is a halogen i.e. F, Cl, Br or I
- General formula is $C_nH_{2n+1}X$ where X is F, Cl, Br or I
- Chloroalkanes and chlorofluoroalkanes (CFCs) can be used as solvents e.g. CCl_4 is used in dry cleaning

2. Preparation from alkanes

- Haloalkanes can be prepared from alkanes by substitution reactions
- Substitution = replacing one atom or group with another atom or group
- The H of an alkane is replaced by Cl or Br e.g.

$$\mathbf{CH_4 + Br_2 \rightarrow CH_3Br + HBr}$$

- More than one H can be replaced e.g.

$$\mathbf{CH_4 + 3Br_2 \rightarrow CHBr_3 + 3HBr}$$

- Requires u/v light to break Br-Br bond
- Mechanism is called **free-radical substitution**

Initiation step	e.g.	$Br_2 \rightarrow 2Br\bullet$		
Propagation	e.g.	$CH_4 + Br\bullet \rightarrow \bullet CH_3 + HBr$	}	as a
		$\bullet CH_3 + Br_2 \rightarrow CH_3Br + Br\bullet$	}	pair
Termination step	e.g.	$2\bullet CH_3 \rightarrow CH_3CH_3$		

3) The ozone layer

- Ultraviolet radiation is harmful to living things. The ozone layer towards the top of the stratosphere absorbs much of the UV from the sun's radiation
- Chlorine atoms catalyse the decomposition of ozone and contribute to the formation of a hole in the ozone layer over Antarctica
- The depletion of the ozone layer has led to increased rates of skin cancer in the Southern hemisphere
- These chlorine atoms are produced by the action of UV light on CFCs (this is sometimes called photolysis)

$$\mathbf{CClF_3 \rightarrow \bullet Cl + \bullet CF_3}$$

- Cl• radicals catalyse the breakdown of stratospheric ozone (by lowering the activation energy for the reaction)

Step 1	$\mathbf{Cl\bullet + O_3}$	$\mathbf{\rightarrow ClO\bullet + O_2}$
Step 2	$\mathbf{ClO\bullet + O_3}$	$\mathbf{\rightarrow Cl\bullet + 2O_2}$
Overall	$\mathbf{2O_3}$	$\mathbf{\rightarrow 3O_2}$

- Cl• does not appear in the overall equation because it is a catalyst (it is used up in step 1 and reformed in step 2)
- Legislation to ban the use of CFCs (Montreal Protocol, 1987) was supported by chemists who have now developed alternative chlorine-free compounds to replace CFCs

4. Substitution Reactions

a) With alkali to form an alcohol

- Reaction is called hydrolysis

- **Example** **$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$**
- Reagents NaOH or KOH
- Conditions Aqueous (dissolved in water)

b) With ammonia to form an amine

- Primary amines contain the functional group $-NH_2$

- **Example** **$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$**
  Ethylamine
- Reagents Excess ammonia
- Conditions Ethanol as solvent

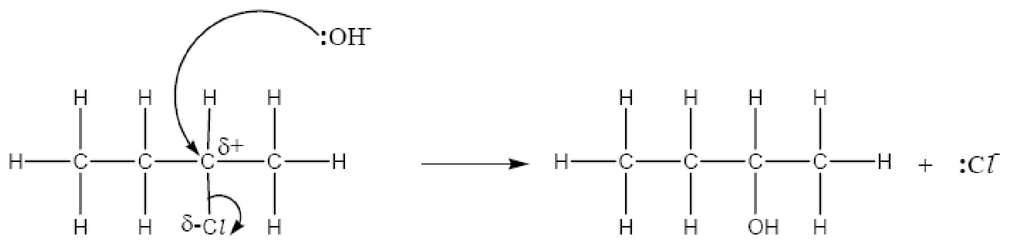
c) With KCN to form a nitrile

- Nitriles contain the functional group ∫N

- **Example** **$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$**
  Propanenitrile
- Reagents NaCN or KCN
- Conditions Warm in aqueous/alcoholic solution

d) Mechanism

- Mechanism is called nucleophilic substitution
- Nucleophiles are attracted to haloalkanes because the C-Hal bond is polar (C is $\delta+$)
- Nucleophile = lone pair donor
- Mechanism includes curly arrows, lone pairs and dipoles



e) Rate of hydrolysis

- Rate of hydrolysis RI > RBr > RCl > RF *because*
- Order of bond strength C-F > C-Cl > C-Br > C-I
- Shown by adding $AgNO_3(aq)$ and timing how long silver halide precipitate takes to form

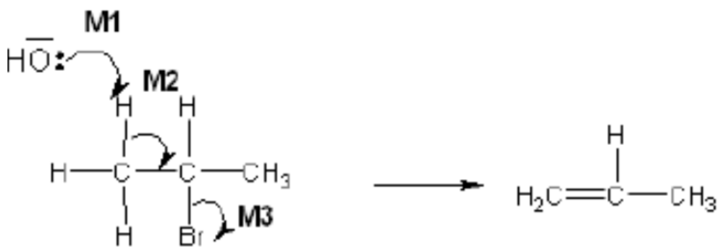
5. Elimination Reactions

Elimination = loss of a small molecule
Instead of acting as a nucleophile, the OH^- acts as a base (removes H^+)

a) With alkali to form an alkene

- Small molecule lost is HBr

- **Example $CH_3CHBrCH_3$ + NaOH $\rightarrow$ CH_2=$CHCH_3$ + NaBr + H_2O**
- Reagents NaOH or KOH
- Conditions Ethanolic (dissolved in ethanol)
- Mechanism:



- This reaction produces an alkene which can be polymerised
- **Haloalkanes and NaOH can do substitution and elimination. To favour elimination, use ethanol as the solvent; to favour substitution, use water as the solvent**