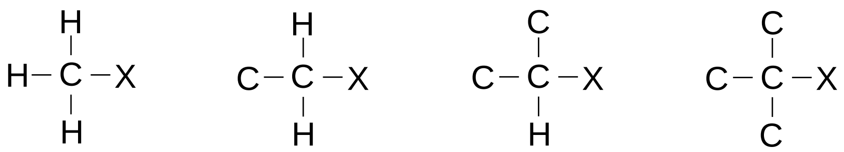
HALOGENOALKANES (HALOALKANES)

Structure Contain the functional group C-X where X is a halogen (F, C*l*, Br or I)

Types **Halogenoalkanes** - halogen is attached to an aliphatic skeleton - alkyl group

Haloarenes - halogen is attached **directly** to a benzene *(aromatic)* ring

Classification Classified according to what is attached to the functional group.



methyl **primary 1°** **secondary 2°** **tertiary 3°**

Names Based on the original alkane with a prefix indicating halogens and their position.

$CH_3CH_2CH_2Cl$ *1-chloropropane* $CH_2ClCHClCH_3$ *1,2-dichloropropane*

$CH_3CHClCH_3$ *2-chloropropane* $CH_3CBr(CH_3)CH_3$ *2-bromo-2-methylpropane*

Q.1 *Draw and name all the structural isomers of $C_3H_6Br_2$, C_4H_9Cl and $C_5H_{11}Br$.*

Q.2 *Classify the structural isomers of C_4H_9Cl and $C_5H_{11}Br$ as 1°, 2° or 3°.*

Physical properties

Boiling points

- **boiling point increases with mass**
- for isomeric compounds the greater the branching, the lower the boiling point

Solubility

- halogenoalkanes are soluble in organic solvents but insoluble in water - *they are not polar enough and don't exhibit hydrogen bonding.*

NUCLEOPHILIC SUBSTITUTION REACTIONS

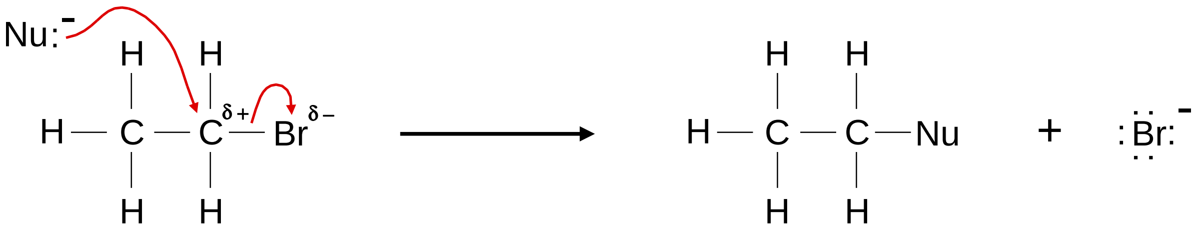
Theory
- halogens have a **greater electronegativity** than carbon
- a **dipole is induced** in the C-X bond and it becomes **polar**
- the carbon is thus open to attack by nucleophiles

$$\overset{\delta+}{C}-\overset{\delta-}{Br}$$

polarity in a C-Br bond

Nucleophiles
- examples are **OH^-**, **CN^-**, **NH_3** and **H_2O**
- possess **at least one LONE PAIR** of electrons
- are **attracted to the slightly positive** (electron deficient) **carbon**

Basic mechanism
- the **nucleophile** uses its lone pair to provide the electrons for a new bond
- as carbon can only have 8 electrons in its outer shell a **halide ion is displaced**
- the result is **substitution** following attack by a nucleophile
- the mechanism is therefore known as - **NUCLEOPHILIC SUBSTITUTION**



Rate of reaction
- the rate of reaction depends on the **strength** not the polarity of the C-X bond

C-I	..238.. **kJmol-1**	*least polar*
C-Br	..276.. **kJmol-1**	↓
C-Cl	..338.. **kJmol-1**	↓
C-F	..484.. **kJmol-1**	*most polar*

WEAKEST BOND
EASIEST TO BREAK
FASTEST REACTION

Practical investigation

The time taken for a precipitate of silver halide is measured. The faster the precipitate forms, the faster the hydrolysis and the weaker the C-X bond.

- warm equal amounts of each halogenoalkane in a water bath
- add a solution of ethanol, water and aqueous silver nitrate to each
- record the time it takes for a precipitate to appear

AgCl - white **AgBr - cream** **AgI - yellow** (AgF is soluble)

NaOH *Reagent* **AQUEOUS** sodium (or potassium) hydroxide

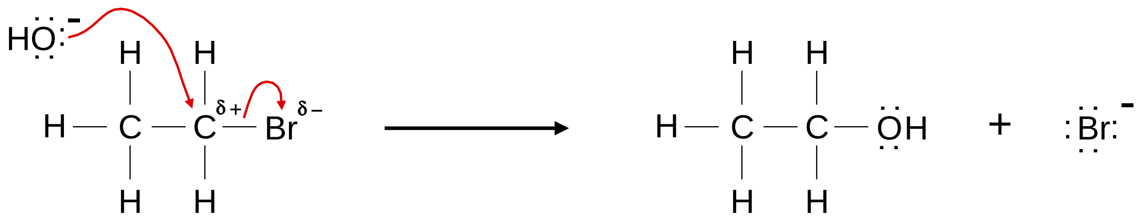
Conditions Reflux in **aqueous** solution (SOLVENT IS IMPORTANT)

Product Alcohol

Nucleophile hydroxide ion (OH^-)

Equation *e.g.* $\mathbf{C_2H_5Br}$(l) + **NaOH**(aq) ——> $\mathbf{C_2H_5OH}$(l) + **NaBr**(aq)

Mechanism



WARNING It is **important to quote the solvent** when answering questions.
Elimination takes place when ethanol is the solvent - SEE LATER

This reaction (and the one with water) is sometimes known as **HYDROLYSIS**

H_2O A similar reaction to that with OH^- takes place with water.
It is **slower** as water is a **poor nucleophile.**

Equation *e.g.* $\mathbf{C_2H_5Br}$(l) + $\mathbf{H_2O}$(l) ——> $\mathbf{C_2H_5OH}$(aq/alc) + **HBr**(aq)

Q.3 *Write equations for the reactions of hot, aqueous NaOH with...*

a) $CH_3CH_2CH_2Br$

b) $CH_3CHBrCH_2CH_3$

c) $(CH_3)_3CBr$

Advanced work

This form of nucleophilic substitution discussed so far is known as S_N2; it is a bimolecular process. An alternative method involves the initial breaking of the C-X bond to form a carbocation, or carbonium ion, (a unimolecular process - S_N1 mechanism), which is then attacked by the nucleophile. S_N1 is favoured for tertiary haloalkanes where there is steric hindrance to the attack and a more stable tertiary, 3°, carbocation intermediate is formed.

USES OF HALOGENOALKANES

Synthetic The reactivity of the C-X bond means that halogenoalkanes play an important part in synthetic organic chemistry. The halogen can be replaced by a variety of groups via a nucleophilic substitution mechanism.

During the **manufacture of ibuprofen**, substitution of a bromine atom takes place.

Monomers **chloroethene** $CH_2 = CHCl$ **tetrafluoroethene** $CF_2 = CF_2$

Polymers

poly(chloroethene)	PVC	$—(CH_2 — CHCl)_n—$	packaging
poly(tetrafluoroethene)	PTFE	$—(CF_2 — CF_2)_n—$	non-stick surfaces

CFC's

dichlorofluoromethane	$CHFCl_2$	refrigerant
trichlorofluoromethane	CF_3Cl	aerosol propellant blowing agent
bromochlorodifluoromethane	$CBrClF_2$	fire extinguishers
	CCl_2FCClF_2	dry cleaning solvent degreasing agent

All the above were chosen because of their..

- low reactivity
- volatility
- non-toxicity

PROBLEMS WITH CFC's

Ozone layer

- CFC's have been blamed for environmental damage by thinning the ozone layer
- Ozone absorbs a lot of harmful UV radiation
- CFC's break up in the atmosphere to form free radicals

$$\mathbf{CF_2Cl_2 \longrightarrow CF_2Cl\bullet + Cl\bullet}$$

- the free radicals catalyse the breaking up of ozone $\mathbf{2O_3 \longrightarrow 3O_2}$

Solution

- CFC's were designed by chemists to help people
- chemists now synthesise **alternatives** to CFC's to protect the environment such as **hydrocarbons** and **HCFC's**
- $\mathbf{CO_2}$ can be use as an **alternative blowing agent**
- this will allow the reversal of the ozone layer problem