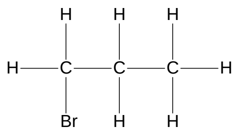
4.2.2 Haloalkanes

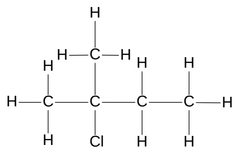
Naming Haloalkanes

Based on original alkane, with a *prefix* indicating halogen atom:
***Fluoro* for F; *Chloro* for Cl; *Bromo* for Br; *Iodo* for I.**

Substituents are listed **alphabetically**



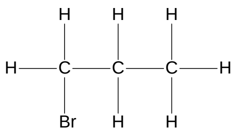
1-bromopropane



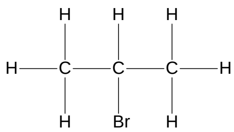
2-chloro-2-methylbutane

Classifying haloalkanes

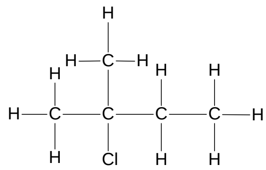
Haloalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



Primary haloalkane
One carbon attached to the carbon atom adjoining the halogen



Secondary haloalkane
Two carbons attached to the carbon atom adjoining the halogen



Tertiary haloalkane
Three carbons attached to the carbon atom adjoining the halogen

Nucleophilic substitution reactions

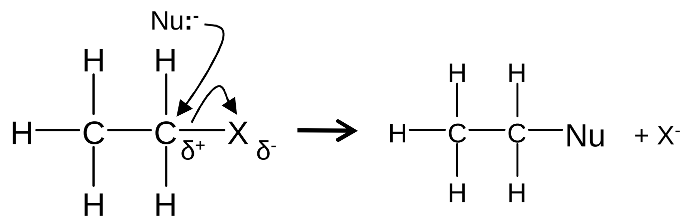
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donator e.g. $:OH^-$, $:NH_3$, CN^-

:Nu represents any nucleophile – they always have a **lone pair** and act as **electron pair donators**

The mechanism: We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

The nucleophiles attack the positive carbon atom



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen

We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

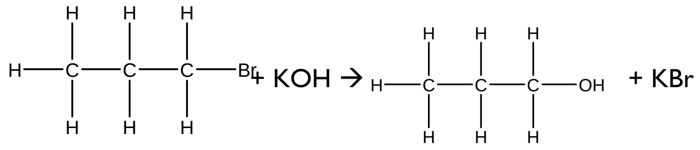
The rate of these substitution reactions depends on the strength of the C-X bond
The weaker the bond, the easier it is to break and the faster the reaction.

	Bond enthalpy / $kJmol^{-1}$
C-I	238
C-Br	276
C-Cl	338
C-F	484

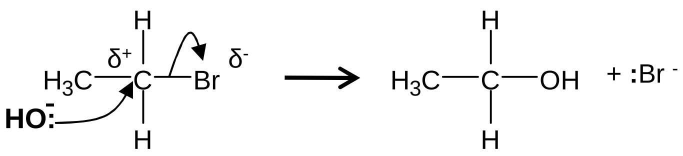
The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

Nucleophilic substitution with ***aqueous*** hydroxide ions

Change in functional group*:*
haloalkane → alcohol
Reagent: potassium (or sodium) hydroxide
Conditions: In **aqueous solution**; Heat under reflux
Mechanism: Nucleophilic substitution
Type of reagent: Nucleophile, OH^-



1-bromopropane propan-1-ol



The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

Comparing the rate of hydrolysis reactions

Hydrolysis is defined as the splitting of a molecule (in this case a haloalkane) by a reaction with water

Water is a **poor nucleophile** but it can react **slowly** with haloalkanes in a substitution reaction. Use reflux OR heat for more than 20 minutes

$$\mathbf{CH_3CH_2X + H_2O \rightarrow CH_3CH_2OH + X^- + H^+}$$

Aqueous silver nitrate is added to a haloalkane and the halide leaving group combines with a silver ion to form a **silver halide precipitate**.
The precipitate only forms when the halide ion has left the haloalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different haloalkanes.

$CH_3CH_2\mathbf{I} + H_2O \rightarrow CH_3CH_2OH + \mathbf{I}^- + H^+$

$Ag^+_{(aq)} + \mathbf{I}^-_{(aq)} \rightarrow Ag\mathbf{I}_{(s)}$ - yellow precipitate

The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

$Ag\mathbf{I}_{(s)}$ - yellow precipitate
$Ag\mathbf{Br}_{(s)}$ – cream precipitate
$Ag\mathbf{Cl}_{(s)}$ – white precipitate
↑ forms faster

Chlorofluorocarbons (CFC's)

CFC's were developed for use as aerosols, refrigerants, and in air-conditioning due their low reactivity, volatility and non-toxicity.

Many of these uses have now been stopped due to the toxicity of haloalkanes and also their detrimental effect on the ozone layer in the atmosphere.

Legislation to ban the use of CFCs was supported by chemists and chemists have now developed alternative chlorine-free compounds.

HFCs (Hydro fluoro carbons) e.g.. CH_2FCF_3 are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond.

CO_2 is now used as a blowing agent for producing expanded polymers instead of CFC's.

The Ozone Layer

The naturally occurring ozone (O_3) layer in the upper atmosphere is beneficial as it filters out much of the sun's harmful UV radiation.

Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog.

Ozone is continuously being formed and broken down in the stratosphere by the action of ultraviolet radiation.

$$O + O_2 \rightleftharpoons O_3$$

Ozone formation
UV light causes an O_2 molecule to split into free radicals

$$O_2 + \text{UV-light} \rightarrow O + O$$

When the free radical hits another O_2 molecule ozone forms

$$O + O_2 \rightarrow \mathbf{O_3}$$

Ozone depletion
This is the reverse of the formation reaction..
The energy is supplied by ultraviolet light

$$O_3 + \text{ultraviolet light} \rightarrow O_2 + O$$

There is a continuous cycle of formation and depletion of ozone

rate of ozone formation = rate of ozone removal

So there is a constant amount of ozone in the atmosphere

The frequency of ultra-violet light absorbed equals the frequency of biologically damaging ultra-violet radiation. These reactions therefore filter out harmful UV and allow life to survive on earth.
UV light can increase risk of skin cancer and increase crop mutation.

Destruction of Ozone Layer

Radicals from CFCs, and NO*x* from thunderstorms or aircraft, may catalyse the breakdown of ozone

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break

$$CF_2Cl_2 \rightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$

The chlorine free radical atoms **catalyse** the decomposition of ozone due to these reactions because they are regenerated. (They provide an alternative route with a lower activation energy)

They contributed to the formation of a hole in the ozone layer.

$$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O^{\bullet} \rightarrow O_2 + Cl^{\bullet}$$

Overall equation

$$O_3 + O^{\bullet} \rightarrow 2\,O_2$$

The regenerated Cl radical means that one Cl radical could destroy many thousands of ozone molecules

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2}$$

$$\mathbf{NO_2 + O^{\bullet} \rightarrow O_2 + NO}$$

Overall equation

$$\mathbf{O_3 + O^{\bullet} \rightarrow 2\,O_2}$$

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CFC's still concern us because CFCs are still entering the atmosphere from disused items and are still used for some purposes and by some countries.

CFCs have a long lifetime in the atmosphere and it takes a long time for CFCs to reach upper atmosphere.