6: Organic Chemistry I

6A. Introduction to Organic Chemistry

**Basic definitions to know**

- **Hydrocarbon** is a compound consisting of hydrogen and carbon only

- **Saturated**: Contain single carbon-carbon bonds only

- **Unsaturated**: Contains a C= C double bond

- **Molecular formula**: The formula which shows the actual number of each type of atom

- **Empirical formula**: shows the simplest whole number ratio of atoms of each element in the compound

- **General formula**: algebraic formula for a homologous series e.g. CnH2n

- **Structural formula** shows the minimal detail that shows the arrangement of atoms in a molecule, eg for butane: CH3CH2CH2CH3 or CH3(CH2)2CH3,

- **Displayed formula**: show all the covalent bonds present in a molecule

**Drawing Displayed formulae**

When drawing organic compounds add the hydrogen atoms so that each carbon has 4 bonds

Remember that the shape around the carbon atom in saturated hydrocarbons is tetrahedral and the bond angle is 109.5°

**Skeletal formula** shows the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional Groups.

- 2-methylbutane
- But-2-ene
- Butan-1-ol
- cyclohexane
- cyclohexene

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Homologous series are families of organic compounds with the same functional group and same general formula.

- They show a gradual change in physical properties (e.g. boiling point).
- Each member differs by CH$_2$ from the last.
- Same chemical properties.

Functional group is an atom or group of atoms which when present in different molecules causes them to have similar chemical properties.

<table>
<thead>
<tr>
<th>homologous series</th>
<th>functional group</th>
<th>prefix / suffix (* = usual use)</th>
<th>example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td></td>
<td>-ane</td>
<td>CH$_3$CH$_2$CH$_2$CH$_3$ Butane</td>
</tr>
<tr>
<td>Alkenes</td>
<td></td>
<td>suffix -ene</td>
<td>propene</td>
</tr>
<tr>
<td>Alcohols</td>
<td></td>
<td>suffix* -ol</td>
<td>Propan-1-ol</td>
</tr>
<tr>
<td></td>
<td>prefix hydroxy-</td>
<td></td>
<td></td>
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<tr>
<td>Halogenoalkanes</td>
<td></td>
<td>prefix chloro-bromo-iodo-</td>
<td>1-chloropropane</td>
</tr>
<tr>
<td>Aldehydes</td>
<td></td>
<td>suffix -al</td>
<td>ethanol</td>
</tr>
<tr>
<td></td>
<td>prefix formyl-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketones</td>
<td></td>
<td>suffix* -one</td>
<td>Propanone</td>
</tr>
<tr>
<td></td>
<td>prefix oxo-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td></td>
<td>suffix -oic acid</td>
<td>Ethanoic acid</td>
</tr>
<tr>
<td>Ester</td>
<td></td>
<td>-yl -oate</td>
<td>methylethanoate</td>
</tr>
</tbody>
</table>

When compounds contain more than one functional group, the order of precedence determines which groups are named with prefix or suffix forms. The highest precedence group takes the suffix (and the lowest number on the carbon chain), with all others taking the prefix form. However, double and triple C-C bonds only take suffix form.

Order of priority highest first:
Carboxylic acids > aldehydes > ketones > alcohols > alkenes > halogenoalkanes
General rules for naming carbon chains

• Count the longest carbon chain and name appropriately
• Find any branched chains and count how many carbons they contain
• Add the appropriate prefix for each branch chain

Eg -CH₃ methyl or -C₂H₅ ethyl –C₃H₇ propyl

<table>
<thead>
<tr>
<th>code</th>
<th>no of carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>meth</td>
<td>1</td>
</tr>
<tr>
<td>eth</td>
<td>2</td>
</tr>
<tr>
<td>prop</td>
<td>3</td>
</tr>
<tr>
<td>but</td>
<td>4</td>
</tr>
<tr>
<td>pent</td>
<td>5</td>
</tr>
<tr>
<td>hex</td>
<td>6</td>
</tr>
<tr>
<td>hept</td>
<td>7</td>
</tr>
<tr>
<td>oct</td>
<td>8</td>
</tr>
<tr>
<td>non</td>
<td>9</td>
</tr>
<tr>
<td>dec</td>
<td>10</td>
</tr>
</tbody>
</table>

3,5-dimethylheptane

Basic rules for naming functional groups

The functional group is named by a prefix or suffix. e.g. bromoethane, ethanol, propene

• When using a suffix, add in the following way:

  If the suffix starts with a vowel - remove the –e from the stem alkane name
  e.g. Propan-1-ol, butan-1-amine, ethanoic acid, ethanoylchloride, butanamide

  If the suffix starts with a consonant or there are two or more of a functional group meaning di, or tri needs to be used then do not remove the the –e from the stem alkane name
  e.g. Propanenitrile, ethane-1,2-diol, propanedioic acid, propane-1,2,3-triol, Pentane-2,4-dione.

• The position of the functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1.

• We only include numbers, however, if they are needed to avoid ambiguity.

• The functional groups take precedence over branched chains in giving the lowest number

  3-methylbut-1-ene is correct and not 2-methylbut-3-ene

• Where there are two or more of the same groups, di-, tri-, tetra-, penta- or hexa- are used. Note the point made above about the addition of ‘e’ to the stem

• Words are separated by numbers with dashes

  CH₂FCCl₂CH₂CH₃ 2,2-dichloro-1-fluorobutane.

• numbers are separated by commas

  CH₂FCH₂CHBrCH₂CH₃ 3-bromo-1-fluoropentane

• If there is more than one functional group or side chain, the groups are listed in alphabetical order (ignoring any di, tri).
Alkenes
The double bond will be between two carbons. Use the lower number of the two to show the position of the double bond

The name for alkenes may include E or Z at start to show the type of stereoisomer

If more than one double bond is present then suffix ends diene or triene. The stem ends in a

The suffix -en for alkenes can go in front of other suffixes. The alcohol and carboxylic acid groups have higher priority than the alkene group so take precedence with numbering

Halogenoalkanes
Class the halogen as a substituent on the C chain and use the suffix -fluoro, -chloro, -bromo, or -iodo. (Give the position number if necessary)

Multiple functional group and side chains are listed in alphabetical order (ignoring any di, tri).

Alcohols
These have the ending -ol and if necessary the position number for the OH group is added between the name stem and the -ol

If there are two or more -OH groups then di, tri are used. Add the ‘e’ on to the stem name though.

The OH group has a higher priority than the halogenoalkane group and alkene so takes precedence in numbering. The OH is on carbon 1
Aldehydes
An aldehyde's name ends in -al
It always has the C=O bond on the first carbon of the chain so it does not need an extra number. It is by default number one on the chain.

If two aldehyde groups then di is put before -al and an e is added to the stem.

Aldehydes have a higher priority than alcohol so the –OH group uses the hydroxy prefix.

Ketones
Ketones end in -one
When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one

If two ketone groups then di is put before –one and an e is added to the stem.

Carboxylic acids
These have the ending -oic acid but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end.

If there are carboxylic acid groups on both ends of the chain then it is called a -dioic acid

Note the e in this name

5-hydroxy-4-methylpentanoic acid
**Isomers**

**Structural isomers**: same molecular formula different structures (or structural formulae)

Structural isomerism can arise from
- Chain isomerism
- Position isomerism
- Functional group isomerism

EDEXCEL does not split structural isomers into the different categories. They are all classed as structural isomers.

**Chain isomers**: Compounds with the same molecular formula but different structures of the carbon skeleton

- Pentane
- 2-methylbutane
- 2,2-dimethylpropane

**Position isomers**: Compounds with the same molecular formula but different structures due to different positions of the same functional group on the same carbon skeleton

- 1-bromopropane
- 2-bromopropane

**Functional group isomers**: Compounds with the same molecular formula but with atoms arranged to give different functional groups

- Ethanol: an alcohol
- Methoxymethane: an ether

- Cyclohexane - cyclo alkane
- Hexene - alkene

Note: Alkene and cyclo alkanes have the same general formula. Hexene and cyclohexane have the same molecular formula but have a different functional group.
Stereoisomerism

Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms.

Alkenes can exhibit a type of isomerism called E-Z stereochemistry.

E-Z isomers exist due to restricted rotation about the C=C bond

Single carbon-carbon covalent bonds can easily rotate

E-Z stereoisomers arise when:
(a) There is restricted rotation around the C=C double bond.
(b) There are two different groups/atoms attached both ends of the double bond.

Naming E-Z stereoisomers
First determine the priority groups on both sides of the double bond

Priority group side 1

Priority group side 2

If the priority atom is on the same side of the double bond it is labelled Z from the German zusammen (The Zame Zide!)

If the priority atom is on the opposite side of the double bond it is labelled E from the German entgegen (The Epposite side!)

cis-trans isomerism is a special case of EIZ isomerism in which two of the substituent groups are the same.
6A Alkanes

Alkanes are saturated hydrocarbons

**General formula** alkane $C_nH_{2n+2}$

**Saturated**: Contain single carbon-carbon bonds only

**Hydrocarbon** is a compound consisting of hydrogen and carbon only

Fuels from crude oil

They are obtained from the crude oil in the order of fractional distillation, cracking and reformation of crude oil

Refining crude oil

**Fractional Distillation:**

Petroleum is a mixture consisting mainly of alkane hydrocarbons

**Petroleum fraction**: mixture of hydrocarbons with a similar chain length and boiling point range

- Oil is pre-heated
- then passed into column.
- The fractions condense at different heights
- The temperature of column decreases upwards
- The separation depends on boiling point.
- Boiling point depends on size of molecules.
- The larger the molecule the larger the London forces
- Similar molecules (size, bp, mass) condense together
- Small molecules condense at the top at lower temperatures
- and big molecules condense at the bottom at higher temperatures.

This is a physical process involving the splitting of weak London forces between molecules

Cracking

**Cracking**: conversion of large hydrocarbons to smaller molecules by breakage of C-C bonds

High Mr alkanes $\rightarrow$ smaller Mr alkanes + alkenes + (hydrogen)

Economic reasons for catalytic cracking

- The petroleum fractions with shorter C chains (e.g. petrol and naphtha) are in **more demand** than larger fractions.
- To make use of excess larger hydrocarbons and to supply demand for shorter ones, longer hydrocarbons are cracked.
- The products of cracking are **more useful and valuable** than the starting materials (e.g. ethene used to make poly(ethene) and ethane-1,2-diol, and ethanol) The smaller alkanes are used for motor fuels which burn more efficiently.

This is a chemical process involving the splitting of strong covalent bonds so requires high temperatures.

Reforming

**Turns straight chain alkanes into branched and cyclic alkanes and Aromatic hydrocarbons**

Branched and cyclic hydrocarbons burn more cleanly and are used to give fuels a higher octane number.

Used for making motor fuels
Alkanes as Fuels

Fuel: releases heat energy when burnt

Complete Combustion
In excess oxygen alkanes will burn with complete combustion

The products of complete combustion are CO₂ and H₂O.

\[
C_8H_{18}(g) + 12.5 O_2(g) \rightarrow 8CO_2(g) + 9 H_2O(l)
\]

Incomplete Combustion
If there is a limited amount of oxygen then incomplete combustion occurs, producing CO (which is very toxic) and/or C (producing a sooty flame)

\[
\begin{align*}
\text{CH}_4(g) + \frac{3}{2} O_2(g) & \rightarrow \text{CO}(g) + 2 H_2O(l) \\
\text{CH}_4(g) + O_2(g) & \rightarrow \text{C}(s) + 2 H_2O(l)
\end{align*}
\]

Carbon monoxide is a highly toxic but odourless gas. It can cause death if it builds up in an enclosed space due to faulty heating appliances.

Pollution from Combustion
Sulfur containing impurities are found in petroleum fractions which produce SO₂ when they are burned.

S + O₂ → SO₂ \quad \text{CH}_3\text{SH} + 3O₂ → SO₂ + CO₂ + 2H₂O

SO₂ is acidic and will dissolve in atmospheric water and can produce acid rain.

Nitrogen Oxides NOₓ
Nitrogen oxides form from the reaction between N₂ and O₂ inside the car engine.
The high temperature and spark in the engine provides sufficient energy to break strong N₂ bond

\[
N_2 + O_2 \rightarrow 2NO \quad N_2 + 2O_2 \rightarrow 2NO_2
\]

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Environmental consequence</th>
</tr>
</thead>
</table>
| Nitrogen oxides (formed when N₂ in the air reacts at the high temperatures and spark in the engine) | NO is toxic and can form smog,
NO₂ is toxic and acidic and forms acid rain |
| Carbon monoxide | toxic |
| Carbon dioxide | Contributes towards global warming |
| Unburnt hydrocarbons (not all fuel burns in the engine) | Contributes towards formation of smog |
| Soot/particulates | Global dimming and respiratory problems |

Catalytic converters
These remove CO, NO, and unburned hydrocarbons (e.g. octane, C₈H₁₈) from the exhaust gases, turning them into ‘harmless’ CO₂, N₂ and H₂O.

\[
\begin{align*}
2 \text{CO} + 2 \text{NO} & \rightarrow 2 \text{CO}_2 + \text{N}_2 \\
C_8H_{18} + 25 \text{NO} & \rightarrow 8 \text{CO}_2 + 12\frac{1}{2} \text{N}_2 + 9 \text{H}_2\text{O}
\end{align*}
\]

Converters have a ceramic honeycomb coated with a thin layer of catalyst metals platinum, palladium, rhodium – to give a large surface area.
## Biofuels

Most fossil fuels come from crude oil, which is a non-renewable resource. Fossil fuel reserves will eventually run out. Alternative fuels have been developed from renewable resources. Alcohols and biodiesel, which can both be made from plants, are two examples of renewable plant-based fuels.

### Advantages of using Biofuels
- Reduction of use of fossil fuels which are finite resources
- Biofuels are renewable
- Use of biodiesel is more carbon-neutral
- Allows fossil fuels to be used as a feedstock for organic compounds
- No risk of large scale pollution from exploitation of fossil fuels

### Disadvantages of Biofuels
- Less food crops may be grown
- Land not used to grow food crops
- Rain forests have to be cut down to provide land
- Shortage of fertile soils

### Alcohol and Biodiesel Production
- **Alcohols such as ethanol can be produced from the fermentation of sugars from plants.**
- **Biodiesel is produced by reacting vegetable oils with a mixture of alkali and methanol.**
Introduction to Mechanisms

To understand how the reaction proceeds we must first understand how bonds are broken in organic mechanisms. There are two ways to break a covalent bond:

**1. HOMOLYTIC FISSION:** *each atom gets one electron from the covalent bond*

When a bond breaks by homolytic fission it forms two **Free Radicals**.

**DEFINITION**

A **Free Radical** is a reactive species which possess an unpaired electron.

**2. HETEROLYTIC FISSION:** *(one atom gets both electrons)*

Most organic reactions occur via heterolytic fission, producing ions.

The Mechanism:

To understand a reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**.

We use curly arrows in mechanisms to show the movement of an electron pair showing either breaking or formation of a covalent bond;

A curly arrow will always start from a **lone pair** of electrons or the **centre of a bond**.
Free Radical Substitution Reactions of Alkanes

Reaction of alkanes with bromine / chlorine in UV light

In the presence of UV light alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

Overall Reaction

\[
\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}
\]

methane chloromethane

This is the overall reaction, but a more complex mixture of products is actually formed.

It proceeds via a series of steps:
- Step one: Initiation
- Step two: Propagation
- Step three: Termination

**Step one Initiation**

Essential condition: UV light

\[
\text{Cl}_2 \rightarrow 2\text{Cl}^* 
\]

The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others as it is the weakest.

UV light does not have enough energy to break the C-H bond

The bond has broken in a process called homolytic fission.

Free Radicals are reactive species which possess an unpaired electron.

Each atom gets one electron from the covalent bond.

**Step two Propagation**

\[
\text{CH}_4 + \text{Cl}^* \rightarrow \text{HCl} + \cdot\text{CH}_3
\]

The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

\[
\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^*
\]

The methyl free radical reacts with a Cl_2 molecule to produce the main product and another Cl free radical.

All propagation steps have a free radical in the reactants and in the products.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a chain reaction.

**Step three Termination**

\[
\cdot\text{CH}_3 + \text{Cl}^* \rightarrow \text{CH}_3\text{Cl}
\]

Collision of two free radicals does not generate further free radicals: the chain is terminated.

\[
\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3 
\]

Minor step leading to impurities of ethane in product.

Write this step using structural formulae and don’t use molecular formulae.
Applying the mechanism to other alkanes

Example: Write mechanism of Br₂ and Propane

The same mechanism is used: Learn the patterns in the mechanism

STEP ONE Initiation

Essential condition: UV light

Br₂ → 2Br⁻ 

Br₂ splits in the same way as Cl₂

STEP TWO Propagation

CH₃CH₂CH₃ + Br⁻ → HBr + CH₃CH₂CH₂⁻ 

Remove one H from the alkane to produce a radical

CH₃CH₂CH₂⁻ + Br₂ → CH₃CH₂CH₂Br + Br⁻ 

To the radical produced in the previous step add a Br

STEP THREE Termination

CH₃CH₂CH₂⁻ + CH₃CH₂CH₂⁻ → CH₃CH₂CH₂CH₂CH₂CH₃

Propagation steps for substituting a halogen on a ‘middle’ carbon

CH₃CH₂CH₃ + Br⁻ → HBr + CH₃CH₂⁺ CH₃ 

If the question asks for the halogen to be substituted onto a middle carbon in the chain, it is important to put the free radical ‘dot’ on the correct carbon in the propagation stages.

CH₃CH⁺CH₃ + Br₂ → CH₃CH₂BrCH₃ + Br⁻ 

Further substitution

Excess Cl₂ present will promote further substitution and could produce CH₂Cl₂, CHCl₃ and CCl₄

These reactions could occur

CH₃Cl + Cl₂ → CH₂Cl₂ + HCl
CH₂Cl₂ + Cl₂ → CHCl₃ + HCl
CHCl₃ + Cl₂ → CCl₄ + HCl

Example propagation steps that would lead to further substitution

CH₃Cl + Cl⁻ → HCl + ·CH₂Cl
·CH₂Cl + Cl₂ → CH₂Cl₂ + Cl⁻

Example 1. Write the overall reaction equation for the formation of CCl₄ from CH₄ + Cl₂

CH₄ + 4 Cl₂ → CCl₄ + 4 HCl

Example 2. Write the overall reaction equation for the formation of CFCl₃ from CH₃F + Cl₂

CH₃F + 3 Cl₂ → CFCl₃ + 3 HCl

Note HCl is always the side product – never H₂

Overall reaction equations

You should be able to write overall reaction equations for various reactions

CH₄ + 4 Cl₂ → CCl₄ + 4 HCl

CH₃F + 3 Cl₂ → CFCl₃ + 3 HCl

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Alkenes are unsaturated hydrocarbons. The general formula is $\text{C}_n\text{H}_{2n}$.

Alkenes contain a carbon-carbon double bond somewhere in their structure.

Ethene: $\text{H}_2\text{C}≡\text{CH}_2$

Propene: $\text{H}_2\text{C}≡\text{C}_2\text{H}_2$

But-1-ene: $\text{H}_2\text{C}≡\text{C}_2\text{H}_4$

But-2-ene: $\text{H}_2\text{C}≡\text{C}_3\text{H}_6$

Numbers need to be added to the name when positional isomers can occur.

$\text{C}≡\text{C}$ double covalent bond consists of one sigma (σ) bond and one pi (π) bond.

π bonds are exposed and have high electron density. They are therefore vulnerable to attack by species which ‘like’ electrons: these species are called electrophiles.

Formation of σ bond:

One $\text{sp}^2$ orbital from each carbon overlap to form a single C-C bond called a sigma (σ) bond.

Rotation can occur around a sigma bond.

Formation of π bond:

The π bond is formed by sideways overlap of two p orbitals on each carbon atom forming a π-bond above and below the plane of the molecule.

The π bond is weaker than the σ bond.

There is restricted rotation about a π bond.

The π bond leads to resultant high electron density above and below the line between the two nuclei.
Addition Reactions of Alkenes

Addition reaction: a reaction where two molecules react together to produce one

1. Reaction of Alkenes with Hydrogen

| Change in functional group: | alkene → alkane |
| Reagent: | hydrogen |
| Conditions: | Nickel Catalyst |
| Type of reaction: | Addition/Reduction |

Electrophilic Addition: Reactions of Alkenes

A π bond is weaker than a σ bond so less energy is needed to break π bond. The π bonds in alkenes are areas with high electron density. This is more accessible to electrophilic attack by electrophiles. Alkenes undergo addition reactions.

2. Reaction of Alkenes with bromine/chlorine

| Change in functional group: | alkene → dihalogenoalkane |
| Reagent: | Bromine (dissolved in organic solvent) |
| Conditions: | Room temperature (not in UV light) |
| Mechanism: | Electrophilic Addition |
| Type of reagent: | Electrophile, Br$^{\delta+}$ |
| Type of Bond Fission: | Heterolytic |

As the Br$_2$ molecule approaches the alkene, the pi bond electrons repel the electron pair in the Br-Br bond. This INDUCES a DIPOLE. Br$_2$ becomes polar and ELECTROPHILIC (Br$^{\delta+}$).

3. Reaction of Hydrogen Bromide with alkenes

| Change in functional group: | alkene → halogenoalkane |
| Reagent: | HCl or HBr |
| Conditions: | Room temperature |
| Mechanism: | Electrophilic Addition |
| Type of reagent: | Electrophile, H$^{\delta+}$ |
| Type of Bond Fission: | Heterolytic |

HBr is a polar molecule because Br is more electronegative than H. The H$^{\delta+}$ is attracted to the electron-rich pi bond.
If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.

But-1-ene will form a mixture of 1-bromobutane and 2-bromobutane on reaction with hydrogen bromide.

![Chemical structures and reactions](image)

**WHY?**
This carbocation intermediate is more stable because the methyl groups on either side of the positive carbon are electron releasing and reduce the charge on the ion which stabilises it.

The order of stability for carbocations is tertiary > secondary > primary.

**In electrophilic addition to alkenes, the major product is formed via the more stable carbocation intermediate.**

In exam answers:
- Draw out both carbocations and identify as primary, secondary and tertiary.
- State which is the more stable carbocation e.g. secondary more stable than primary.
- State that the more stable carbocation is stabilised because the methyl groups on either (or one) side of the positive carbon are electron releasing and reduce the charge on the ion.
- (If both carbocations are secondary then both will be equally stable and a 50/50 split will be achieved.)

---

### 4. Reaction of Potassium Manganate(VII) with Alkenes

- **Change in functional group:** alkene → diol
- **Reagent:** KMnO₄ in an acidified solution
- **Conditions:** Room temperature
- **Type of reaction:** Oxidation
- **Observation:** purple colour of MnO₄⁻ ion will decolourise to colourless

![Chemical reaction](image)

This reaction with its colour change can be used as a test for the alkene functional group. It would not change colour with alkanes.

### 5. Reaction of Bromine Water with Alkenes

- **Reagent:** Bromine dissolved in water
- **Conditions:** Room temperature
- **Type of reaction:** Addition
- **Observation:** Orange colour of bromine water will decolourise to colourless

![Chemical reaction](image)

This reaction with its colour change is used as a test for the alkene functional group.
**Hydration of alkenes to form alcohols**

Industrially alkenes are converted to alcohols in one step rather than the two in the above sulfuric acid reaction. They are reacted with water in the presence of an acid catalyst.

\[ \text{CH}_2=\text{CH}_2 (g) + \text{H}_2\text{O} (g) \rightarrow \text{CH}_3\text{CH}_2\text{OH} (l) \]

The high pressures needed mean this cannot be done in the laboratory. It is preferred industrially, however, as there are no waste products and so has a high atom economy. It would also mean separation of products is easier (and cheaper) to carry out. See equilibrium chapter for more on the industrial conditions for this reaction.

**Essential Conditions**
- High temperature 300 to 600°C
- High pressure 70 atm
- Catalyst of concentrated H₃PO₄

**Addition Polymers**

Addition polymers are formed from alkenes

This is called **addition polymerisation**

**Poly(alkenes) like alkanes are unreactive due to the strong C-C and C-H bonds.**

**Add the n’s if writing an equation showing the reaction where ‘n’ monomers become ‘n’ repeating units**

**Poly(ethene):** is used to make plastics bags, buckets, bottles. It is a flexible, easily moulded, waterproof, chemical proof, and low density plastic.

**Poly(propene):** is a stiffer polymer, used in utensils and containers and fibres in rope and carpets.

You should be able to draw the polymer repeating unit for any alkene
e.g. For but-2-ene

\[ \text{H}_3\text{C} = \text{CH} = \text{CH} - \text{CH}_3 \rightarrow \begin{bmatrix} \text{H} \\ \text{C} \\ \text{C} \\ \text{H} \\ \text{CH}_3 \\ \text{CH}_3 \end{bmatrix} \]
Methods of disposal of waste Polymers

**Incineration**
Rubbish is burnt and energy produced is used to generate electricity. Some toxins can be released on incineration. (e.g. Combustion of halogenated plastics (ie PVC) can lead to the formation of toxic, acidic waste products such as HCl.) Modern incinerators can burn more efficiently and most toxins and pollutants can be removed. Greenhouse gases will still be emitted though. Volume of rubbish is greatly reduced.

**Recycling**
Saves raw materials - nearly all polymers are formed from compounds sourced/produced from crude oil. Saves precious resources. Polymers need collecting/ sorting - expensive process in terms of energy and manpower. Polymers can only be recycled into the same type – so careful separation needs to be done. Thermoplastic polymers can be melted down and reshaped.

**feedstock for cracking**
Polymers can be cracked into small molecules which can be used to make other chemicals and new polymers - Saves raw materials-

Chemists have designed ways to remove toxic waste products like HCl before they are emitted into the atmosphere. The waste gases from the incinerator are scrubbed/reacted with a base or carbonate. The base reacts with the acidic HCl gas, neutralising it (eg CaO + 2HCl → CaCl₂ + H₂O)

Chemists have also develop biodegradable and compostable polymers. Biodegradable polymers can be made from substances such as maize and starch.
6D Halogenoalkanes

Naming Halogenoalkanes

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

Classifying Halogenoalkanes

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

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

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

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

Reactions of Halogenoalkanes

Nucleophilic substitution reactions

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

Nucleophile: electron pair donator e.g. :OH, :NH₃, CN⁻

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

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.

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

<table>
<thead>
<tr>
<th>Bond enthalpy / kJmol⁻¹</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C-I</td>
<td>238</td>
</tr>
<tr>
<td>C-Br</td>
<td>276</td>
</tr>
<tr>
<td>C-Cl</td>
<td>338</td>
</tr>
<tr>
<td>C-F</td>
<td>484</td>
</tr>
</tbody>
</table>

Halogenoalkanes undergo either substitution or elimination reactions

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

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

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

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Comparing the rate of hydrolysis reactions

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

$$
\text{CH}_3\text{CH}_2\text{X} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{X}^- + \text{H}^+
$$

**Aqueous silver nitrate** is added to a halogenoalkane 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 halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

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.

**Water** is a *poor nucleophile* but it can react *slowly* with halogenoalkanes in a substitution reaction.

$$
\text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{I}^- + \text{H}^+
$$

Aqueous silver nitrate is added to a halogenoalkane and the halide leaving group combines with a silver ion to form a *silver halide 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 aqueous conditions needed is an important point. If the solvent is changed to *ethanol* an elimination reaction occurs.

**Nucleophilic substitution with aqueous hydroxide ions**

<table>
<thead>
<tr>
<th>Change in functional group: halogenoalkane → alcohol</th>
<th>Reagent: potassium (or sodium) hydroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions: In <em>aqueous solution</em>: Heat under reflux</td>
<td>Mechanism: Nucleophilic Substitution</td>
</tr>
<tr>
<td>Role of reagent: Nucleophile, OH⁻</td>
<td></td>
</tr>
</tbody>
</table>

The OH⁻ is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the C⁺⁺.

**SN₂ nucleophilic substitution mechanism for halogenoalkanes**

This mechanism occurs with primary halogenoalkanes.

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**SN<sub>1</sub> nucleophilic substitution mechanism for tertiary halogenoalkanes**

Tertiary haloalkanes undergo nucleophilic substitution in a different way

![SN1 mechanism diagram]

The Br first breaks away from the haloalkane to form a carbocation intermediate. The hydroxide nucleophile then attacks the positive carbon.

Primary haloalkanes do not do the SN<sub>1</sub> mechanism because they would only form an unstable primary carbocation.

**Nucleophilic substitution with ammonia**

*Change in functional group: halogenoalkane → amine*

Reagent: NH₃ dissolved in ethanol
Conditions: Heating under pressure in a sealed tube
Mechanism: Nucleophilic Substitution
Type of reagent: Nucleophile, :NH₃

![Nucleophilic substitution with ammonia diagram]

In the above example, propylamine, the propyl shows the 3 C’s of the carbon chain. Sometimes it is easier to use the IUPAC naming for amines e.g. Propan-1-amine.

Further substitution reactions can occur between the haloalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.
Elimination reaction of halogenoalkanes

Elimination with alcoholic hydroxide ions

<table>
<thead>
<tr>
<th>Change in functional group: halogenoalkane → alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagents: Potassium (or sodium) hydroxide</td>
</tr>
<tr>
<td>Conditions: In ethanol; Heat</td>
</tr>
<tr>
<td>Mechanism: Elimination</td>
</tr>
<tr>
<td>Role of reagent: Base, OH^-</td>
</tr>
</tbody>
</table>

![Chemical reaction diagram]

Elimination: removal of small molecule (often water) from the organic molecule

\[
\text{1-bromopropane} + \text{KOH} \rightarrow \text{propene} + \text{KBr} + \text{H}_2\text{O}
\]

Note the importance of the solvent to the type of reaction here.

**Aqueous:** substitution

**Alcoholic:** elimination

Often a mixture of products from both elimination and substitution occurs.

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed.

![Structural isomer diagram]

The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

Uses of halogenoalkanes

Halogenoalkanes have been used as refrigerants, fire retardants, pesticides and aerosol propellants.

Chloroalkanes and chlorofluoroalkanes can be used as solvents.

\(\text{CH}_3\text{CCl}_3\) was used as the solvent in dry cleaning

Some halogenoalkanes have low flammability.

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer.
6E Alcohols

General formula alcohols $C_nH_{2n+1}OH$

**Naming Alcohols**

These have the ending -ol and if necessary the position number for the OH group is added between the name stem and the -ol.

If the compound has an -OH group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix hydroxy-:

If there are two or more -OH groups then di, tri are used. Add the 'e' on to the stem name though.

**Bond angles in Alcohols**

All the H-C-H bonds and C-C-O are 109.5° (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.

The H-O- C bond is 104.5° (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

**Different types of alcohols**

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen.

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen.

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen.
1. Combustion of Alcohols

Alcohols combust with a clean flame

\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \]

2. Reaction of Alcohols with Sodium

Sodium reacts with alcohols

\[ 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{Na} \rightarrow 2\text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+ + \text{H}_2 \]

This reaction can be used as a test for alcohols

Observations:
- effervescence,
- the mixture gets hot,
- sodium dissolves,
- a white solid is produced.

3. Substitution reactions of Alcohols to form Halogenoalkanes

Various halogenating compounds can be used to substitute the –OH group for a halogen

**Reaction with phosphorous (V) halide**

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{POCl}_3 + \text{HCl} \]

This reaction with \( \text{PCl}_5 \) (phosphorous(V)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.

**For Br use KBr, 50% concentrated H_2SO_4 to produce HBr**

**Reaction with phosphorous (III) iodide**

\[ \text{PI}_3 + 3 \text{CH}_3\text{CH}_2\text{OH} \rightarrow 3\text{CH}_3\text{CH}_2\text{I} + \text{H}_3\text{PO}_3 \]

The phosphorous (III) iodide is produced in situ by reacting red phosphorus and iodine.

The reaction of KI and conc H_2SO_4 can’t be used to produce HI because the sulfuric acid will oxidise the hydrogen halides to other products.

4. Oxidation reactions of the alcohols

Potassium dichromate \( \text{K}_2\text{Cr}_2\text{O}_7 \) is an oxidising agent that causes alcohols to oxidise.

**Partial Oxidation of Primary Alcohols**

**Reaction**: primary alcohol \( \rightarrow \) aldehyde

**Reagent**: potassium dichromate (VI) solution and dilute sulfuric acid.

**Conditions**: (use a limited amount of dichromate) warm gently and *distil* out the aldehyde as it forms:

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}(\text{CH}_3)-\text{OH} + \text{[O]} & \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)-\text{CHO} + \text{H}_2\text{O} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{[O]} & \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}
\end{align*}
\]

An aldehyde's name ends in \(-\text{al}\)

It always has the \( \text{C}=\text{O} \) bond on the first carbon of the chain so it does not need an extra number

Observation: the orange dichromate ion \( (\text{Cr}_2\text{O}_7^{2-}) \) reduces to the green \( \text{Cr}^{3+} \) ion
Full Oxidation of Primary Alcohols

Reaction: primary alcohol → carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid
Conditions: use an excess of dichromate, and heat under reflux: (distil off product after the reaction has finished)

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O}
\]

Oxidation of Secondary Alcohols

Reaction: secondary alcohol → ketone
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid.
Conditions: heat under reflux

There is no further oxidation of the ketone under these conditions.

Tertiary alcohols cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

Distinguishing between Aldehydes and Ketones

The fact that aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised is the chemical basis for tests that are commonly used to distinguish between aldehydes and ketones

Fehling’s (Benedict’s) solution
Reagent: Fehling’s solution containing blue Cu^{2+} ions.
Conditions: heat gently
Reaction: aldehydes only are oxidised by Fehling’s solution into a carboxylic acid and the copper (II) ions are reduced to copper(I) oxide
Observation: Aldehydes: Blue Cu^{2+} ions in solution change to a red precipitate of Cu_{2}O. Ketones do not react

\[
\text{CH}_3\text{CHO} + 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{Cu}_2\text{O} + 4\text{H}^+
\]
Reaction of Alcohols with Dehydrating Agents

**Reaction:** Alcohol → Alkene

**Reagents:** Concentrated phosphoric acid

**Conditions:** warm (under reflux)

**Role of reagent:** dehydrating agent/catalyst

**Type of reaction:** acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule

![Chemical diagram showing the dehydration of propan-1-ol to yield propene](image)

\[
\text{propan-1-ol} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Propene} + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \xrightarrow{} \quad \text{CH}_2=\text{CHCH}_3 + \text{H}_2\text{O}
\]

Some \text{2}^{\text{nd}} and \text{3}^{\text{rd}} alcohols can give more than one product, when the double bond forms between different carbon atoms.

Butan-2-ol can form both alkenes although more but-2-ene would be formed.

But-2-ene could also exist as E and Z isomers.

Producing alkenes from alcohols provides a possible route to polymers without using monomers derived from oil.
### Organic techniques

#### Distillation

In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

**Classic AS reaction using distillation**

**Reaction:** primary alcohol $\rightarrow$ aldehyde  
**Reagent:** potassium dichromate (VI) solution and dilute sulfuric acid.  
**Conditions:** use a limited amount of dichromate and warm gently and distil out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]  
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$  
**Observation**  
Orange dichromate solution changes to green colour of $\text{Cr}^{3+}$ ions  

---

#### Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

**Never seal the end of the condenser** as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated.

**Classic AS reaction using reflux**

**Reaction:** primary alcohol $\rightarrow$ carboxylic acid  
**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid  
**Conditions:** use an excess of dichromate, and **heat under reflux:** (distil off product after the reaction has finished using distillation set up)  
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{O}$  
**Observation**  
Orange dichromate solution changes to green colour of $\text{Cr}^{3+}$ ions  

---

Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles.

---

It’s important to be able to draw and label this apparatus accurately.  
- Don’t draw lines between flask and condenser.  
- Don’t have top of condenser sealed  
- Condenser must have outer tube for water that is sealed at top and bottom  
- Condenser must have two openings for water in and out that are open

---

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.
Purifying an organic liquid

• Put the distillate of impure product into a separating funnel

• Wash product by adding either
  • sodium hydrogen carbonate solution, shaking and releasing the pressure from CO₂ produced.
  • Saturated sodium chloride solution

• Allow the layers to separate in the funnel, and then run and discard the aqueous layer.

• Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulfate) to dry the organic liquid.

• Carefully decant the liquid into the distillation flask

• Distil to collect pure product

Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer.
Distil to separate oil from organic solvent
Add anhydrous CaCl₂ to clove oil to dry oil
Decant to remove CaCl₂

Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

Sodium hydrogen carbonate will neutralise any remaining reactant acid.
Sodium chloride will help separate the organic layer from the aqueous layer.

The drying agent should
• be insoluble in the organic liquid
• not react with the organic liquid

Separating funnel