7. AS mechanisms

- **poly(alkene)**
  - high pressure
  - Catalyst
  - polymerization

- **alkene**
  - \( \text{Br}_2, \text{Cl}_2 \)
  - room temp
  - Electrophilic addition

- **alcohol**
  - If primary
    - \( \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+ \)
    - heat gently and distill
    - partial oxidation
  - If secondary
    - \( \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+ \)
    - heat under reflux
    - oxidation

- **aldehyde**
  - (If primary)
    - \( \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+ \)
    - heat under reflux
    - excess oxidising agent
    - Oxidation

- **ketone**
  - \( \text{KMnO}_4 \)
  - oxidation

- **halogenoalkane**
  - KOH aqueous
  - heat under reflux
  - Nucleophilic substitution

- **dihalogenoalkane**
  - KOH aqueous
  - heat under reflux
  - Nucleophilic substitution

- **diol**
  - UV light
  - Free radical Substitution

- **alkane**
  - \( \text{H}_2 \)
  - Nickel Catalyst
  - addition/reduction

- **amine**
  - Alcoholic \( \text{NH}_3 \)
  - heat under pressure
  - Nucleophilic substitution

- **poly(alkene)**
  - **alkene**
  - **alcohol**
  - **aldehyde**
  - **ketone**
  - **carboxylic acid**
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

   ![Homolytic Fission Diagram]

   The bond has broken in a process called homolytic fission.

   When a bond breaks by homolytic fission it forms two **Free Radicals**. **Free Radicals** do not have a charge and are represented by a \( \bullet \).

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

   ![Heterolytic Fission Diagram]

   Two headed arrow shows movement of pair of electrons.

   Heterolytic fission produces **IONS**.

   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**.

![Mechanism Diagram]

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

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

Electrophile: an electron pair acceptor
Nucleophile: electron pair donor e.g. :OH⁻, :NH₃, CN⁻

Electrophilic Addition Reactions of Alkenes

A π bond is weaker than a σ bond so less energy 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.

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⁺
Type of Bond Fission: Heterolytic

As the Br₂ molecule approaches the alkene, the π bond electrons repel the electron pair in the Br-Br bond. This INDUCES a DIPOLE. Br₂ becomes polar and ELECTROPHILIC (Br⁺).

The INTERMEDIATE formed, which has a positive charge on a carbon atom is called a CARBOCATION.

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⁺
Type of Bond Fission: Heterolytic

HBr is a polar molecule because Br is more electronegative than H. The H⁺ is attracted to the electron-rich π 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.

![Carbocation Intermediate Diagram]

**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)

**Nucleophilic substitution reactions**

The nucleophiles attack the positive carbon atom.

- We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons.
- :Nu represents any nucleophile – they always have a lone pair and act as electron pair donators.
- 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.

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>
Nucleophilic substitution with *aqueous* hydroxide ions

<table>
<thead>
<tr>
<th>Change in functional group: halgenoalkane $\rightarrow$ alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent: potassium (or sodium) hydroxide</td>
</tr>
<tr>
<td>Conditions: In <em>aqueous solution</em>: Heat under reflux</td>
</tr>
<tr>
<td>Mechanism: Nucleophilic Substitution</td>
</tr>
<tr>
<td>Role of reagent: Nucleophile, OH$^-$.</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$^{\delta^+}$

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

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**SN$_2$** nucleophilic substitution mechanism for halogenoalkanes

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**SN$_1$** nucleophilic substitution mechanism for tertiary halogenoalkanes

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Primary halogenoalkanes don’t do the SN$_1$ mechanism because they would only form an unstable primary carbocation.
Nucleophilic substitution with ammonia

**Change in functional group:** halogenoalkane → amine  
Reagent: NH$_3$, dissolved in ethanol  
Conditions: Heating under pressure in a sealed tube  
Mechanism: Nucleophilic Substitution  
Type of reagent: Nucleophile, :NH$_3$

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

**DEFINITION**

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

**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.

**DEFINITION**

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

The bond has broken in a process called **homolytic fission**.

\[
\text{Cl} \quad \text{Cl} \rightarrow \text{Cl}^+ \quad \text{Cl}^-
\]

**DEFINITION**

*each* atom gets one electron from the covalent bond

When a bond breaks by homolytic fission it forms **Free Radicals**.  
**Free Radicals** do not have a charge and are represented by a •

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.
STEP TWO Propagation

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

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

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

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

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

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

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 Br\(_2\) and Propane

STEP ONE Initiation

Essential condition: UV light

\[ \text{Br}_2 \rightarrow 2\text{Br}^\cdot \]

Br\(_2\) splits in the same way as Cl\(_2\).

STEP TWO Propagation

\[ \text{CH}_2\text{CH}_3 + \text{Br}^\cdot \rightarrow \text{HBr} + \text{CH}_2\text{CH}_2\text{CH}_2^\cdot \]

Remove one H from the alkane to produce a radical.

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

To the radical produced in the previous step add a Br.

STEP THREE Termination

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

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

Further substitution

Excess Cl\(_2\) present will promote further substitution and could produce CH\(_2\)Cl\(_2\), CHCl\(_3\) and CCl\(_4\).

These reactions could occur

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

Example propagation steps that would lead to further substitution

\[ \cdot\text{CH}_2\text{Cl} + \text{Cl}^\cdot \rightarrow \text{HCl} + \cdot\text{CH}_2\text{Cl} \]
\[ \cdot\text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}^\cdot \]
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 is continuously being formed and broken down in the stratosphere by the action of ultraviolet radiation.

$\text{O} + \text{O}_2 \rightleftharpoons \text{O}_3$

Ozone formation
UV light causes an $\text{O}_2$ molecule to split into free radicals:
$\text{O}_2 + \text{UV-light} \rightarrow \text{O} + \text{O}$
When the free radical hits another $\text{O}_2$ molecule ozone forms:
$\text{O} + \text{O}_2 \rightarrow \text{O}_3$

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

Ozone depletion
This is the reverse of the formation reaction:
The energy is supplied by ultraviolet light:
$\text{O}_3 + \text{ultraviolet light} \rightarrow \text{O}_2 + \text{O}$

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.

Destruction of Ozone Layer

Radicals from CFCs, and $\text{NOx}$ from thunderstorms or aircraft, may catalyse the breakdown of ozone.

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.

Aircraft releasing NO is a problem because they release it closer to the ozone layer

$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
$\text{NO}_2 + \text{O}^* \rightarrow \text{O}_2 + \text{NO}$
Overall equation:
$\text{O}_3 + \text{O}^* \rightarrow 2 \text{O}_2$

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

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.

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break. The C-F bond is much harder to break than the C-Cl bond.

$\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl}^* + \text{Cl}^*$

$\text{Cl}^* + \text{O}_3 \rightarrow \text{ClO}^* + \text{O}_2$
$\text{ClO}^* + \text{O}^* \rightarrow \text{O}_2 + \text{Cl}^*$
Overall equation:
$\text{O}_3 + \text{O}^* \rightarrow 2 \text{O}_2$

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

HFCs (Hydro fluoro carbons) e.g. $\text{CH}_2\text{FCF}_3$ are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond.