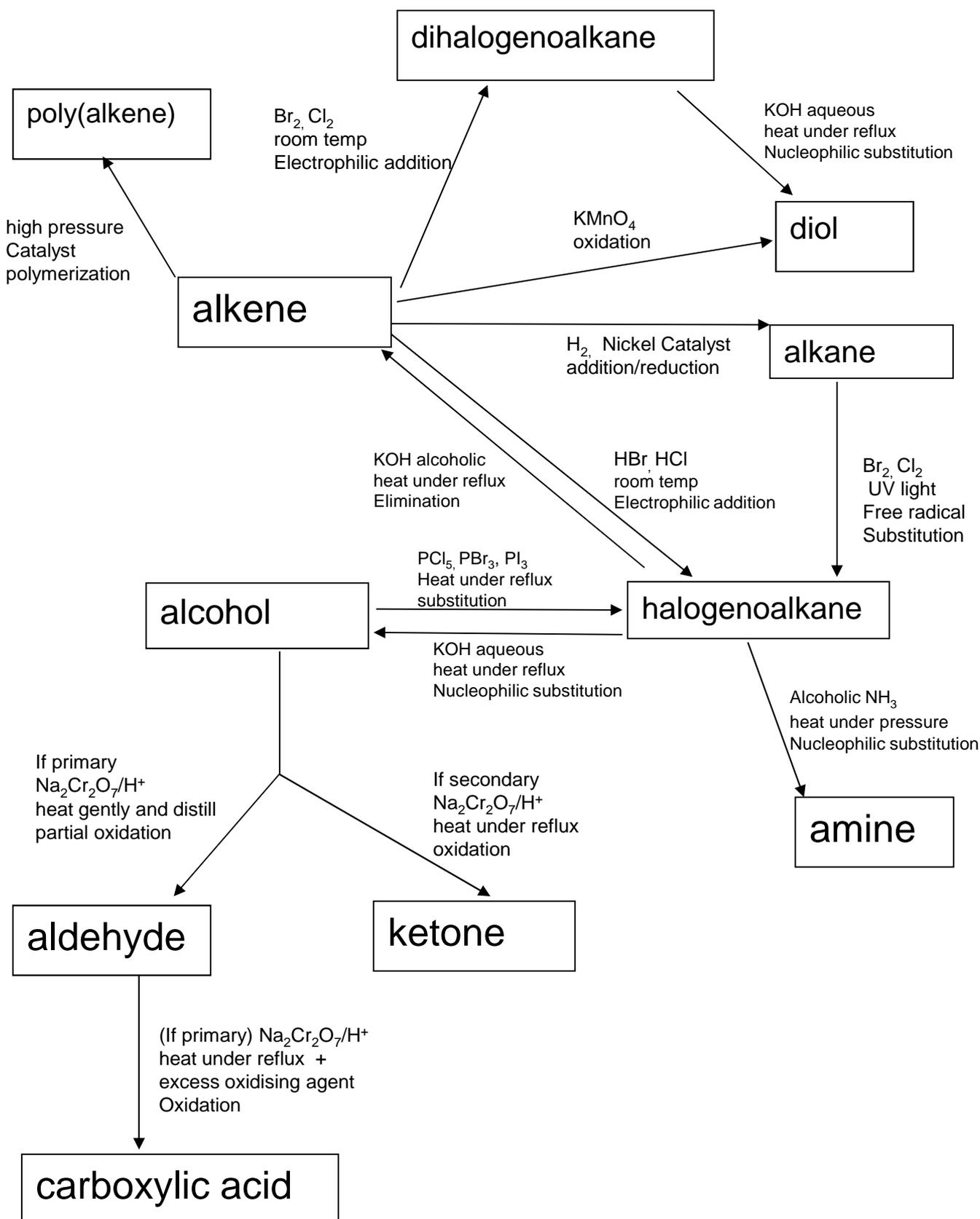


## 7. AS mechanisms

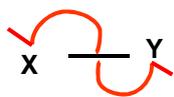


## Introduction to mechanisms

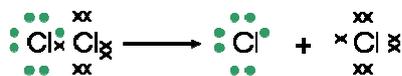
To understand how the reaction proceeds we must first understand how bonds are broken in organic mechanisms  
There are two ways to break a covalent bond:

### 1. HOMOLYTIC FISSION:

*each atom gets **one** electron from the covalent bond*



one headed arrow shows movement of one electron



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

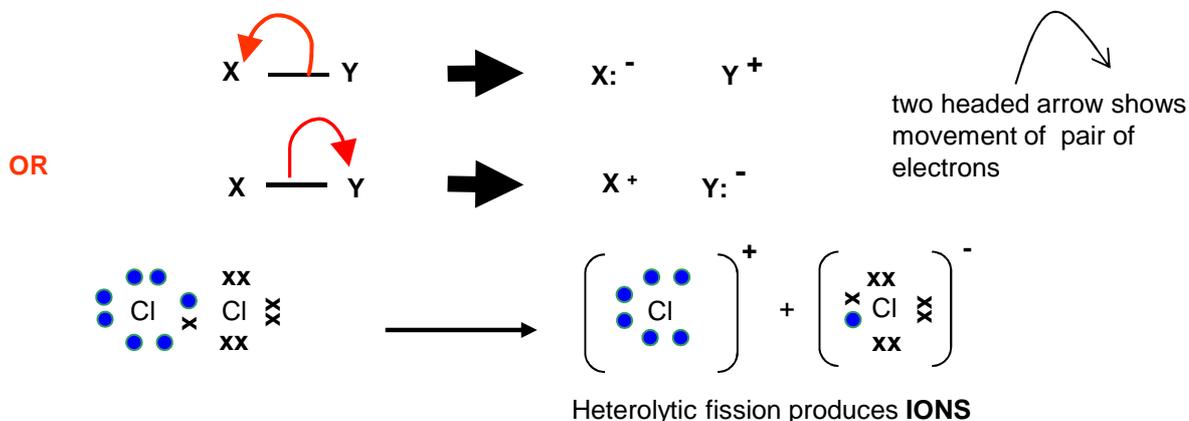
When a bond breaks by homolytic fission it forms two **Free Radicals**.

**Free Radicals** do not have a charge and are represented by a  $\cdot$

#### DEFINITION

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

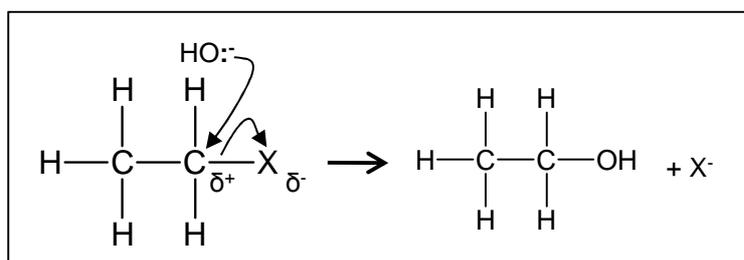
### 2. HETEROLYTIC FISSION: (*one atom gets **both** electrons*)



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**



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**

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

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

**Definition** Electrophile: an **electron pair acceptor**

Nucleophile: electron pair donator e.g.  $\text{:OH}^-$ ,  $\text{:NH}_3$ ,  $\text{CN}^-$

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

## Electrophilic Addition Reactions of Alkenes

A  $\pi$  bond is weaker than a  $\sigma$  bond so less energy needed to break  $\pi$  bond

The  $\pi$  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  $\rightarrow$  dihalogenoalkane

**Reagent:** Bromine (dissolved in organic solvent)

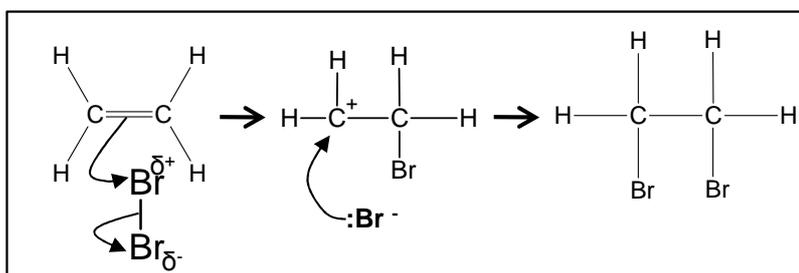
**Conditions:** Room temperature (not in UV light)

**Mechanism:** Electrophilic Addition

**Type of reagent:** Electrophile,  $\text{Br}^{\delta+}$

**Type of Bond Fission:** Heterolytic

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



The **INTERMEDIATE** formed, which has a positive charge on a carbon atom is called a **CARBICATION**

### Reaction of hydrogen bromide with alkenes

**Change in functional group:** alkene  $\rightarrow$  halogenoalkane

**Reagent:** HCl or HBr

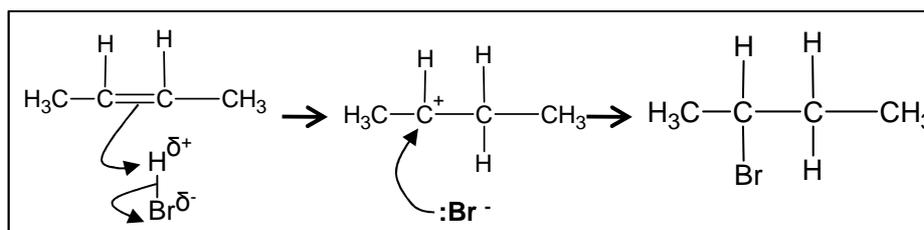
**Conditions:** Room temperature

**Mechanism:** Electrophilic Addition

**Type of reagent:** Electrophile,  $\text{H}^{\delta+}$

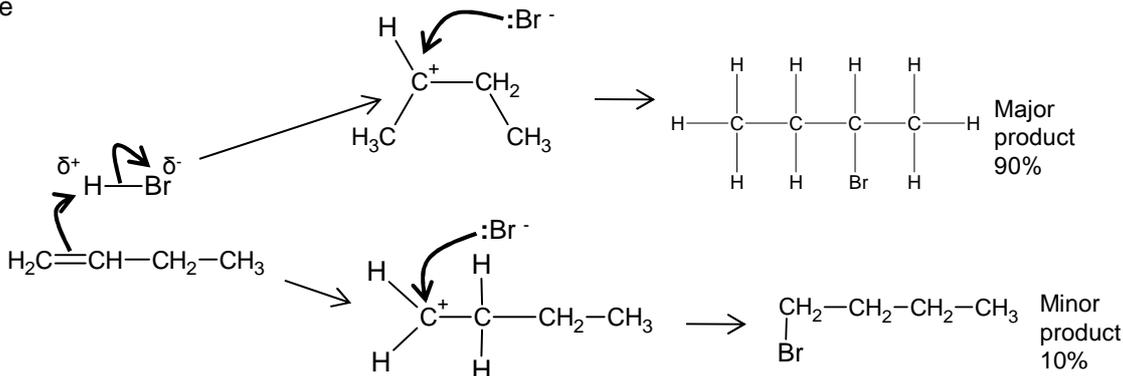
**Type of Bond Fission:** Heterolytic

HBr is a polar molecule because Br is more electronegative than H. The  $\text{H}^{\delta+}$  is attracted to the electron-rich pi bond.



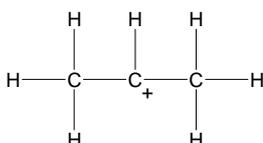
If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.

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



### 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.



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

In exam answers

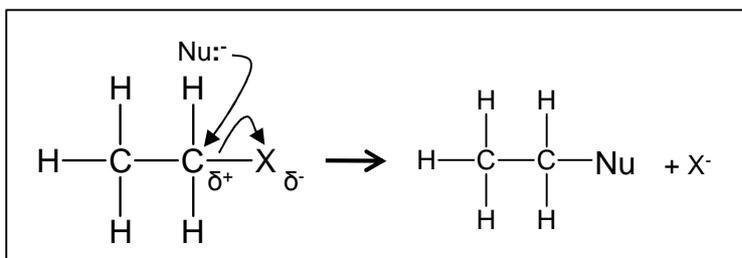
- Draw out both carbocations and identify as primary, secondary and tertiary
- State which is the more stable carbocation e.g. secondary more stable than primary
- State that the more stable carbocation is stabilised because the methyl groups on either (or one) side of the positive carbon are electron 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)

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

## Nucleophilic substitution reactions

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

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.

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

	Bond enthalpy / kJmol <sup>-1</sup>
C-I	238
C-Br	276
C-Cl	338
C-F	484

## Nucleophilic substitution with aqueous hydroxide ions

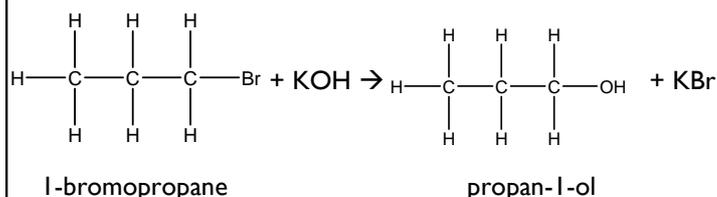
**Change in functional group:** halogenoalkane → alcohol

**Reagent:** potassium (or sodium) hydroxide

**Conditions:** In aqueous solution; Heat under reflux

**Mechanism:** Nucleophilic Substitution

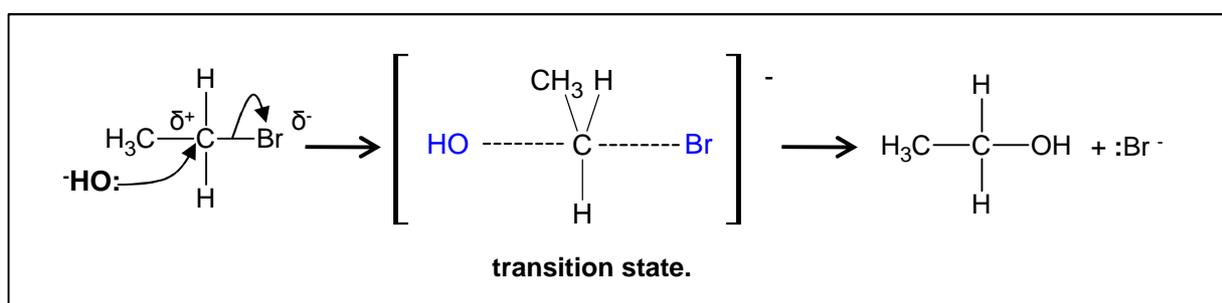
**Role of reagent:** Nucleophile, OH<sup>-</sup>



The OH<sup>-</sup> is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the C<sup>δ+</sup>

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

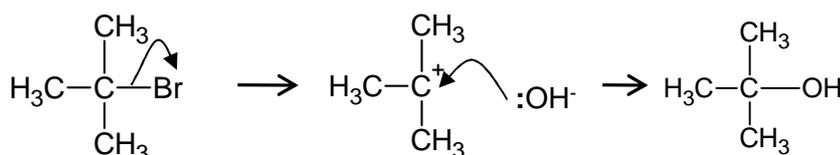
### SN<sub>2</sub> nucleophilic substitution mechanism for halogenoalkanes



This mechanism occurs with primary halogenoalkanes

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

Tertiary haloalkanes undergo nucleophilic substitution in a different way



The Br first breaks away from the haloalkane to form a carbocation intermediate

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is made stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above

Primary halogenoalkanes don't do the SN<sub>1</sub> mechanism because they would only form an unstable primary carbocation.

## Nucleophilic substitution with ammonia

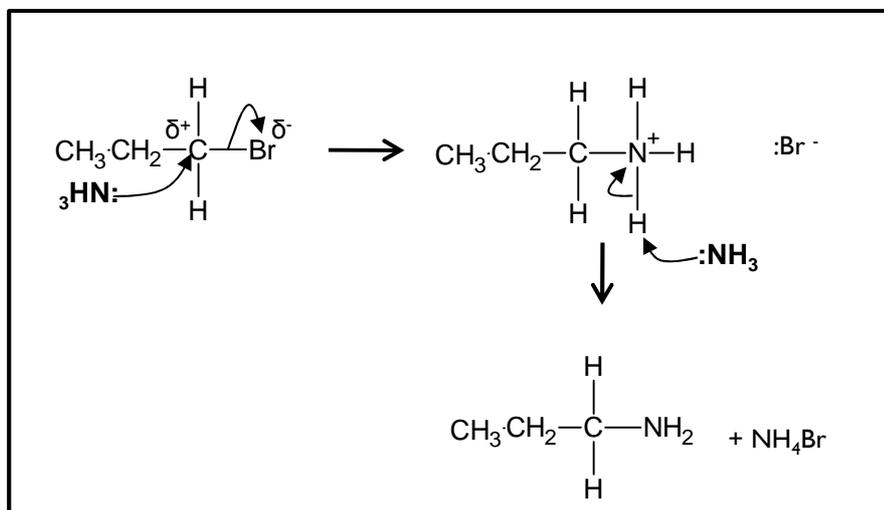
**Change in functional group:** halogenoalkane → amine

**Reagent:**  $\text{NH}_3$  dissolved in ethanol

**Conditions:** Heating under pressure in a sealed tube

**Mechanism:** Nucleophilic Substitution

**Type of reagent:** Nucleophile,  $:\text{NH}_3$

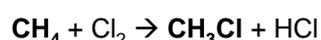


## Free Radical Substitution Reactions of Alkanes

**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**



methane      chloromethane

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

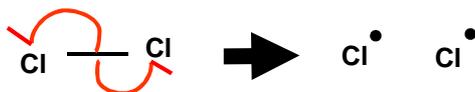
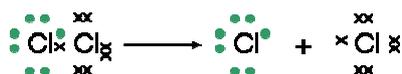
In general, alkanes do not react with many reagents. This is because the C-C bond and the C-H bond are relatively strong

The **MECHANISM** for this reaction is called a **FREE RADICAL SUBSTITUTION**

It proceeds via a series of steps:  
STEP ONE: **Initiation**  
STEP TWO: **Propagation**  
STEP THREE: **Termination**

### STEP ONE Initiation

Essential condition: UV light



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**.

*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  $\bullet$

### DEFINITION

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

### STEP TWO Propagation



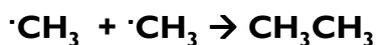
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a  $\text{Cl}_2$  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



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  $\text{Br}_2$  and Propane

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

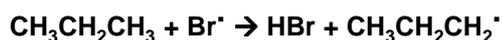
#### STEP ONE Initiation

Essential condition: UV light



$\text{Br}_2$  splits in the same way as  $\text{Cl}_2$

#### STEP TWO Propagation

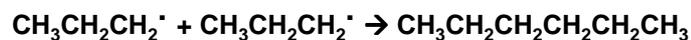


← Remove one H from the alkane to produce a radical



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

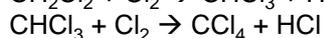
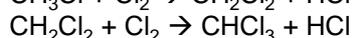
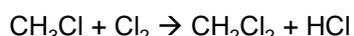
#### STEP THREE Termination



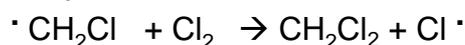
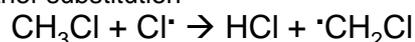
### Further substitution

Excess  $\text{Cl}_2$  present will promote further substitution and could produce  **$\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$**

These reactions could occur



Example propagation steps that would lead to further substitution



## The Ozone Layer

The naturally occurring ozone (O<sub>3</sub>) layer in the upper atmosphere is beneficial as it filters out much of the sun's harmful UV radiation

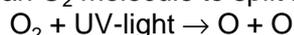
Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog

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

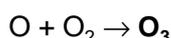


### Ozone formation

UV light causes an O<sub>2</sub> molecule to split into free radicals



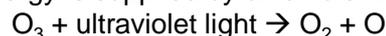
When the free radical hits another O<sub>2</sub> molecule ozone forms



### Ozone depletion

This is the reverse of the formation reaction..

The energy is supplied by ultraviolet light



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 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.

## Destruction of Ozone Layer

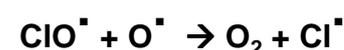
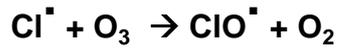
Radicals from CFCs, and NO<sub>x</sub> from thunderstorms or aircraft, may catalyse the breakdown of ozone

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

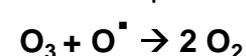


The chlorine free radical atoms **catalyse** the decomposition of ozone due to these reactions because they are regenerated. (They provide an alternative route with a lower activation energy)

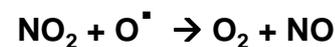
They contributed to the formation of a hole in the ozone layer.



Overall equation



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



Overall equation



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

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

HFCs (Hydro fluoro carbons) e.g. CH<sub>2</sub>FCF<sub>3</sub> are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond

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.