HL IB Chemistry

Electron Pair Sharing Reactions

Contents

Nucleophilic Substitution

Nucleophilic Substitution

What is a nucleophile?

- A **nucleophile** is an electron-rich species that can **donate** a pair of electrons
  - 'Nucleophile' means 'nucleus/positive charge loving' as nucleophiles are attracted to positively charged species
  - **Nucleophilic** refers to reactions that involve a nucleophile
- There are various different species which can behave as nucleophiles, and some make better nucleophiles than others

A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge

Examples of neutral and charged nucleophiles

Neutral	Charged
H_2O	OH^-
NH_3	Cl^-
ROH	CN^-
RNH_2	R^- (carbanions)

- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile
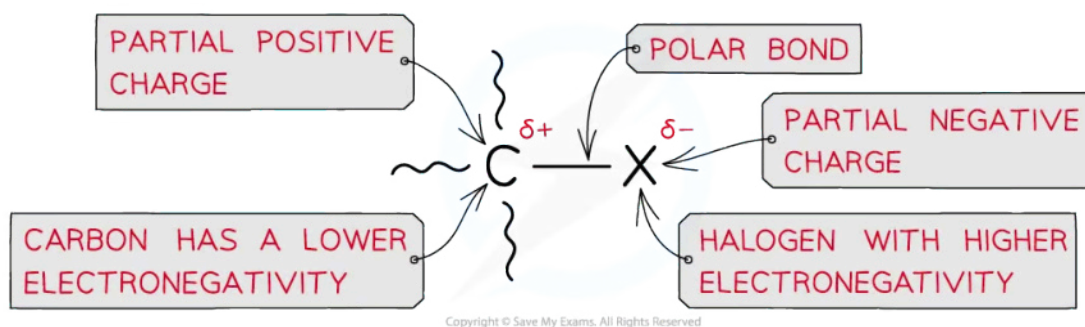
Equations for Nucleophilic Substitution

- Haloalkanes will undergo nucleophilic substitution reactions due to the polar C–X bond (where X is a halogen)

Partial positive C atom and partial negative X atom

PARTIAL POSITIVE CHARGE

POLAR BOND

$\delta+$ $\delta-$

PARTIAL NEGATIVE CHARGE

C — X

CARBON HAS A LOWER ELECTRONEGATIVITY

HALOGEN WITH HIGHER ELECTRONEGATIVITY

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Due to large differences in electronegativity between the carbon and halogen atom, the C–X bond is polar

Diagram to show nucleophilic substitution where :Nu⁻ represents the nucleophile

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General Mechanism for Nucleophilic Substitution

Hydrolysis of Haloalkanes

- The nucleophile in this reaction is the hydroxide, OH^- ion
- An **aqueous** solution of **sodium hydroxide** (NaOH) or **potassium hydroxide** (KOH) with **ethanol** is used
- This reaction is very slow at room temperature, so the reaction mixture is warmed
- This is an example of a **hydrolysis reaction** and the product is an alcohol

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + :Br^-$$

bromoethane → ethanol
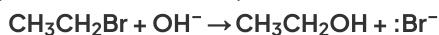
- $:Br^-$ is the leaving group
  - Halogens make good leaving groups as they form relatively weak bonds with carbon
  - Their higher electronegativity also means the bonded electrons are drawn towards the halogen atom making the carbon partially positive, $\delta+$, and susceptible to nucleophilic attack
- The rate of this reaction depends on the type of halogen in the haloalkane

- The stronger the C–X bond, the slower the rate of the reaction
- In terms of bond enthalpy, C–F > C–Cl > C–Br > C–I
- Fluoroalkanes do not react at all, but iodoalkanes have a very fast rate of reaction

The nucleophilic substitution mechanisms for the above reactions are as follows:

### Nucleophilic substitution mechanism of bromoethane with a hydroxide ion

Nucleophilic Substitution with OH⁻, the bond that forms and the bond that breaks must both involve the carbon atom that is bonded to the leaving group

Neutral nucleophiles

- When the nucleophile is neutral, e.g. H_2O, the initial product is positive
- The positive product then deprotonates, losing H^+, and forms a neutral product
  - $CH_3CH_2Cl + H_2O \rightarrow CH_3CH_2OH + :H^+$

Diagram to show water acting as a nucleophile forming a positive product which is then deprotonated
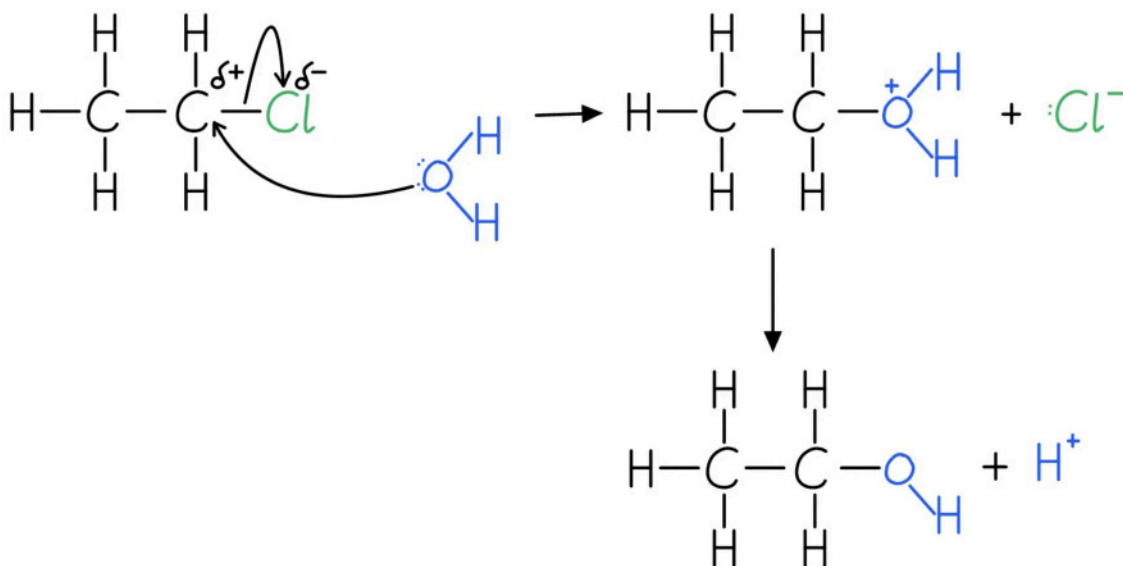
*Nucleophilic substitution reactions with neutral nucleophiles involves deprotonation*
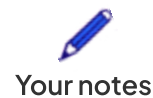
Heterolytic Fission

Heterolytic Fission

Heterolytic fission

- Heterolytic fission is breaking a covalent bond in such a way that the more electronegative atom takes both the electrons from the bond to form a negative ion and leaves behind a positive ion

Diagram to show the process of heterolytic fission
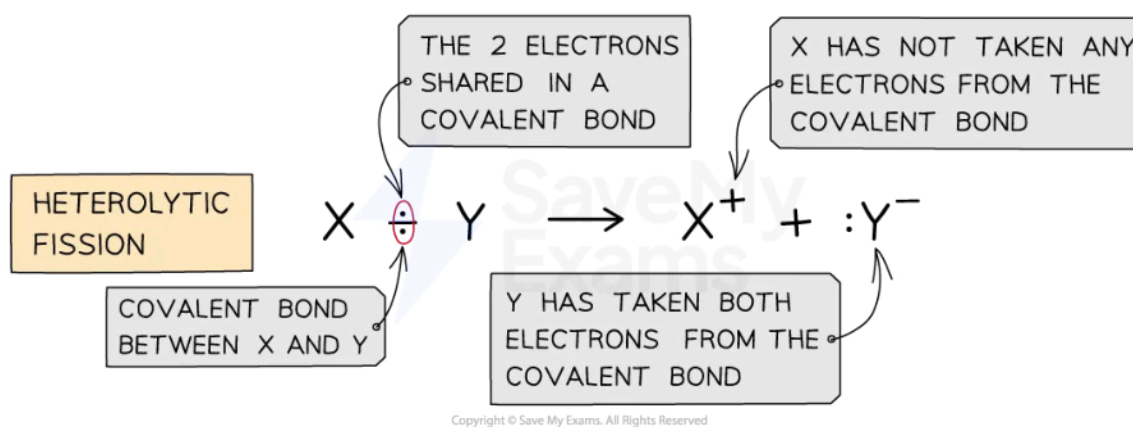
*Heterolytic fission forms a positive ion and a negative ion*

- In heterolytic fission, a double-headed arrow is used to show the movement of a **pair of electrons**
- The resulting negative ion is an electron-rich species that can **donate** a pair of electrons
  - This makes the negative ion a **nucleophile**
- The resulting positive ion is an electron-deficient species that can **accept** a pair of electrons
  - This makes the positive ion an **electrophile**

Heterolytic fission mechanism

Your notes
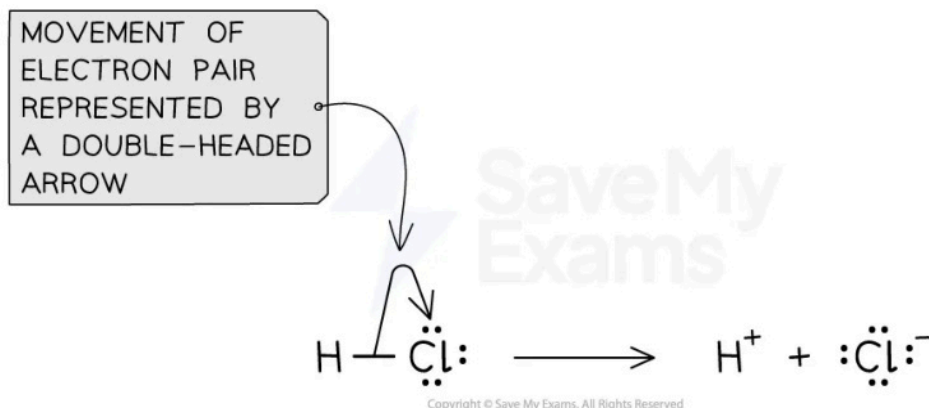
- The opposite reaction to heterolytic fission occurs when a nucleophile donates a pair of electrons to the electrophile forming a coordination bond

Reaction between a nucleophile and an electrophile forming a coordination bond
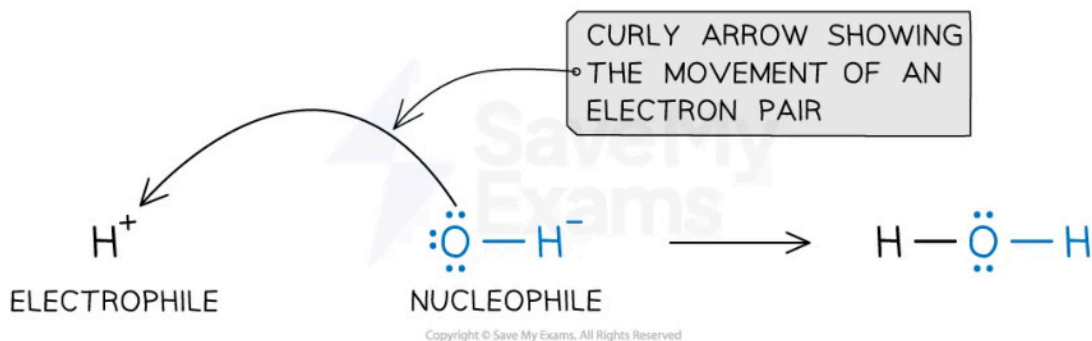
A nucleophile 'loves' a positive charge and an electrophile 'loves' a negative charge

Electrophilic Addition Reactions

Electrophiles

What is an electrophile?

- An electrophile is a species that forms a covalent bond when reacted with a nucleophile by accepting electrons
- They are electron-deficient so will have a positive charge or partial positive charge

Examples of neutral and charged electrophiles

| Neutral	Charged (cations)
HX (hydrogen halides)	H^+
X_2 (halogens)	NO_2^+
H_2O	NO^+
RX (halogenoalkanes)	R^+

Electrophilic Addition Reactions

- **Electrophilic addition** is the addition of an electrophile to an alkene double bond, C=C
- The alkene double bond, C=C, is an area of high electron density which makes it susceptible to attack by electrophiles
- The C=C bond breaks forming a single C-C bond and 2 new bonds from each of the two carbon atoms
- Electrophilic addition reactions include the addition of:
    - Steam, H_2O (g) to form alcohols
    - Hydrogen halides, HX , to form halogenoalkanes
    - Halogens, X_2, to form dihalogenoalaknes

Why does the C=C bond react with electrophiles?

- Alkenes are unsaturated molecules that contain a C=C bond
- The atoms around the carbon-carbon double bond adopt a **planar arrangement** and the bond angle is 120°

Diagram to show the planar arrangement of the C=C bond
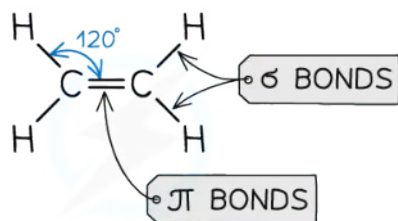
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The bond angles are 120°

- The presence of the **C=C** bond gives **alkenes** a number of chemical properties that are not seen in **alkanes**
- Since the **alkene** contains **π–bonds**, it is possible to break the weaker **π–bond** and form stronger **σ–bonds** with other species without forcing any atoms on the molecule to break off
- As a result **alkenes** (unlike **alkanes**) are capable of undergoing **addition reactions**
- The ability of **alkenes** to undergo **addition** means that they are much **more reactive** than **alkanes**

### Diagram to show the general equation for addition reactions across the C=C
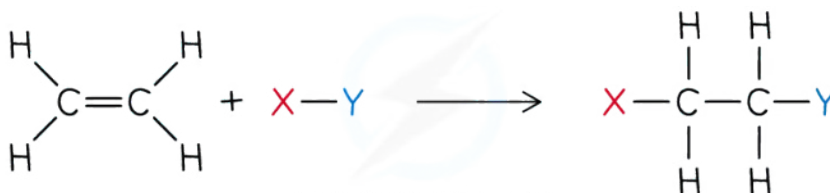
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Addition reactions in alkenes

Addition of water

Your notes

- When alkenes are treated with steam at **300 ºC,** a pressure of **60 atmospheres** and **sulfuric acid (H$_2$SO$_4$)** or **phosphoric acid (H$_3$PO$_4$)** catalyst, the water is added across the double bond in a reaction known as **hydration**
- An **alkene** is converted into an **alcohol**
- The reaction processes via an intermediate in which H$^+$ and HSO$_4^-$ ions are added across the **double bond**
- The intermediate is quickly hydrolysed by water, reforming the sulfuric acid
- The following equation shows the conversion of ethene to ethanol

$$CH_2CH_2 \xrightarrow[\text{H}_2\text{O}]{\text{H}_2\text{SO}_4} CH_3CH_2OH$$
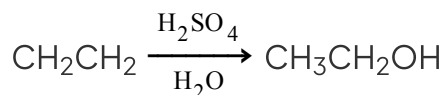
$$\text{ethene} \qquad \text{ethanol}$$

- This is a very important industrial reaction for producing large quantities of ethanol, a widely used solvent and fuel
- The process is much faster and higher yielding that producing ethanol by **fermentation**

Addition of halogens

- The reaction between **alkenes** and halogens is known as **halogenation**
- It is an example of an **electrophilic addition** where an electrophile ('electron seeker') joins onto to a double bond
- The C=C double bond is broken, and a new single bond is formed from each of the two carbon atoms
- The result of this reaction is a **dihalogenoalkane**

This reaction occurs readily at room temperature and is the basis for the test for unsaturation in molecules

Halogenation in alkenes

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contain a double bond)
- Br$_2$ is an orange or yellow solution, called **bromine water**
- The unknown compound is **shaken** with the bromine water
- If the compound is unsaturated, an addition reaction will take place and the coloured solution will decolourise

Diagram to show the colour change that occurs when testing for unsaturation
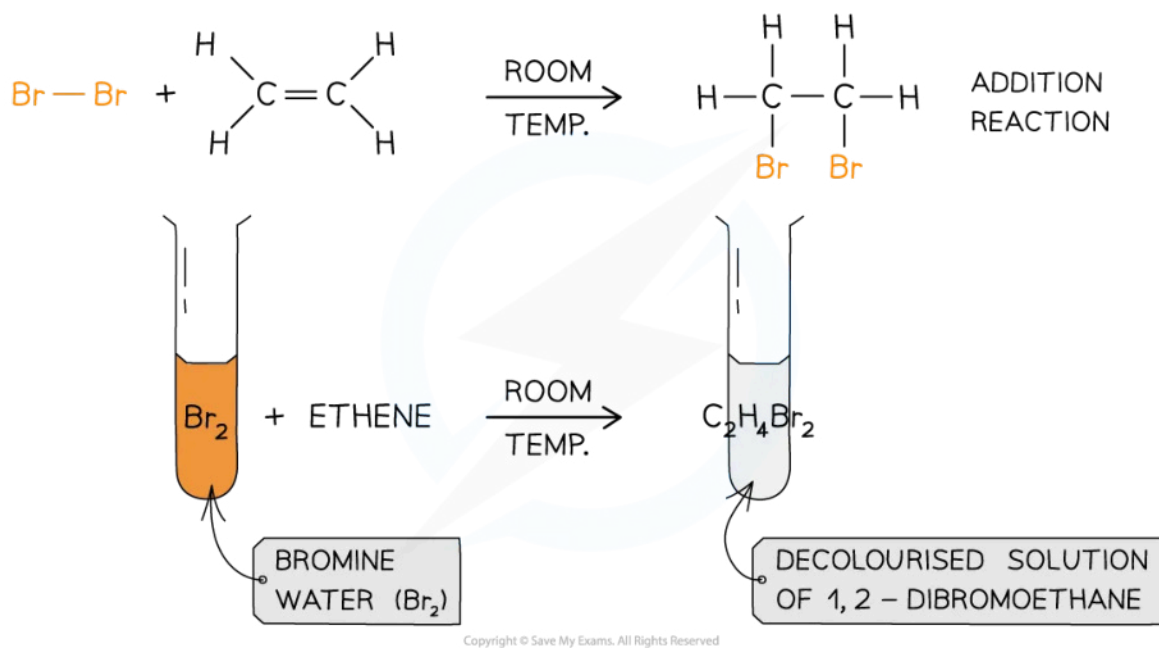
The bromine water test is the standard test for unsaturation in alkenes

Addition of hydrogen halides

- **Alkenes** will react readily with **hydrogen halides** such as **HCl** and **HBr** to produce **halogenoalkanes**
- This reaction is known as **hydrohalogenation**
- It is also an **electrophilic addition** reaction that occurs quickly at room temperature

Formation of a halogenoalkane from an alkene and hydrogen halide

Hydrohalogenation reactions in alkenes

- All the **hydrogen halides** react in this way, but the **fastest reaction** occurs in the order **HI > HBr > HCl** due to the increasing bond strength of the hydrogen-halogen bond, so the weakest bond reacts most easily
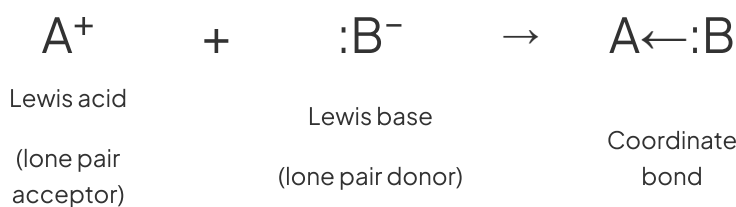
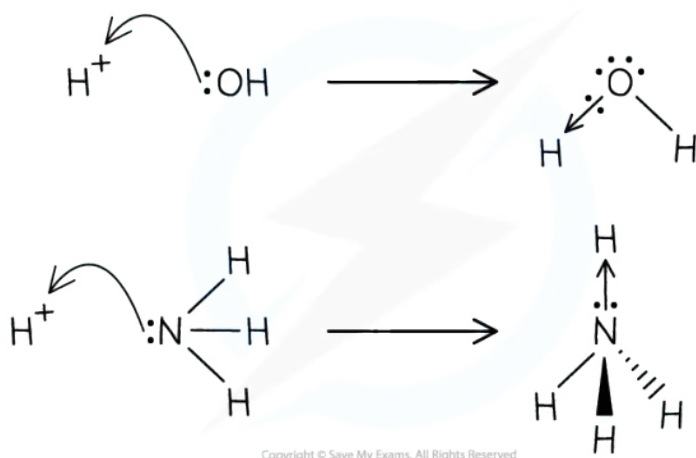## Lewis Acids & Bases (HL)

Lewis Acids & Bases

A more general definition of acids and bases was given by G.N. Lewis who defined them as:

- A Lewis **acid** is an **lone pair acceptor**
- A Lewis **base** is an **lone pair donor**
- The general mechanism for Lewis acids and bases can be represented as:

$$A^+ \quad + \quad :B^- \quad \rightarrow \quad A \leftarrow :B$$

Lewis acid
(lone pair acceptor)

Lewis base
(lone pair donor)

Coordinate bond

- This enabled a wider range of substances to be classed as acids or bases
- This can be shown in the following examples in which a hydroxide ion, OH^-, and ammonia, NH_3, donate a lone pair to a hydrogen ion

Diagram to show how OH^- and ammonia act as Lewis bases

The OH^- ion and ammonia act as Lewis bases in both examples by donating a lone pair of electrons

## How are Brønsted-Lowry Acids and Bases Different from Lewis Acids and Bases?

- A **Brønsted-Lowry acid** is a species that can donate H^+
- For example, hydrogen chloride (HCl) is a Brønsted-Lowry acid as it can donate a H^+ ion

$$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$$
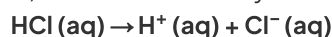
- Lewis acids, by definition, covers a boarder spectrum than Brønsted-Lowry acids
- Lewis acids are any compounds that are able to accept a lone pair of electrons which includes H^+ itself
- Brønsted-Lowry acid and base theory considers acids as H^+ **donors only**
- This does not of course occur in every reaction

- A **Brønsted-Lowry base** is a species that can accept H^+
  - For example, a hydroxide (OH^-) ion is a Brønsted-Lowry base as it can accept H^+ to form water
- Lewis bases and Brønsted-Lowry bases are in the same group of compounds as both of these must have a lone pair of electrons
- The following molecules can behave as either Lewis bases and Brønsted-Lowry bases
  - Lewis bases as they can donate an electron pair
  - Brønsted-Lowry base as they can accept a proton

Hydroxide, cyanide and methylamine
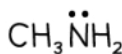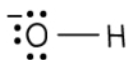
Examples of molecules that can behave both as Lewis bases and Brønsted–Lowry base

Lewis Acid & Base Reactions (HL)

Lewis Acid & Base Reactions

Formation of coordinate bonds

- When ammonia, NH_3, and boron trifluoride, BF_3, react a coordinate bond is formed
- This occur as the lone pair on the nitrogen atom in NH_3 can be donated to the boron atom in BF_3, creating a molecule of NH_3BF_3
- NH_3 reacts as a Lewis base as is donates a lone pair of electrons and BF_3 acts as a Lewis acid
- Only electron pairs are being donated and accepted
- In this case, neither compound reacts as an Brønsted-Lowry acid or Brønsted-Lowry base as no protons (H^+ ions) are being donated or accepted

Diagram showing boron trifluoride acting as a Lewis acid and ammonia acting as a Lewis base
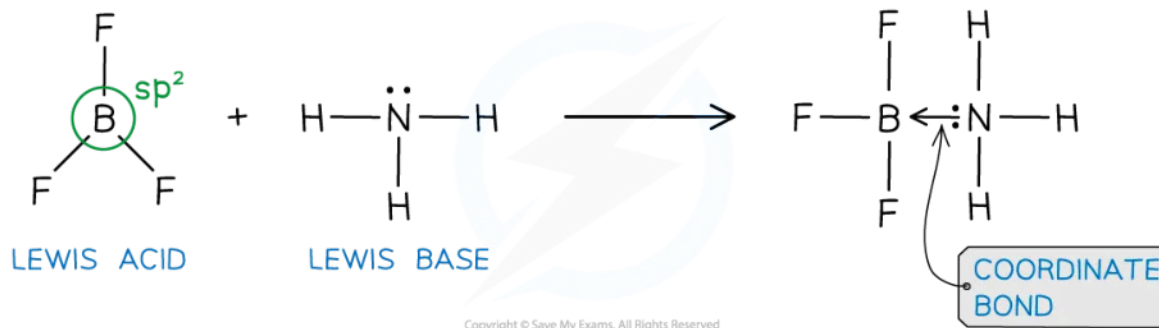
Ammonia donates a lone pair of electrons to form a coordinate bond

- Here boron forms three sp^2 hybridised orbitals leaving a vacant $2p_z$ orbital which allows the lone pair on the nitrogen atom to form a dative covalent bond

Boron forms three sp^2 hybridised orbitals

SPACE FOR A LONE PAIR TO FORM COORDINATE BOND
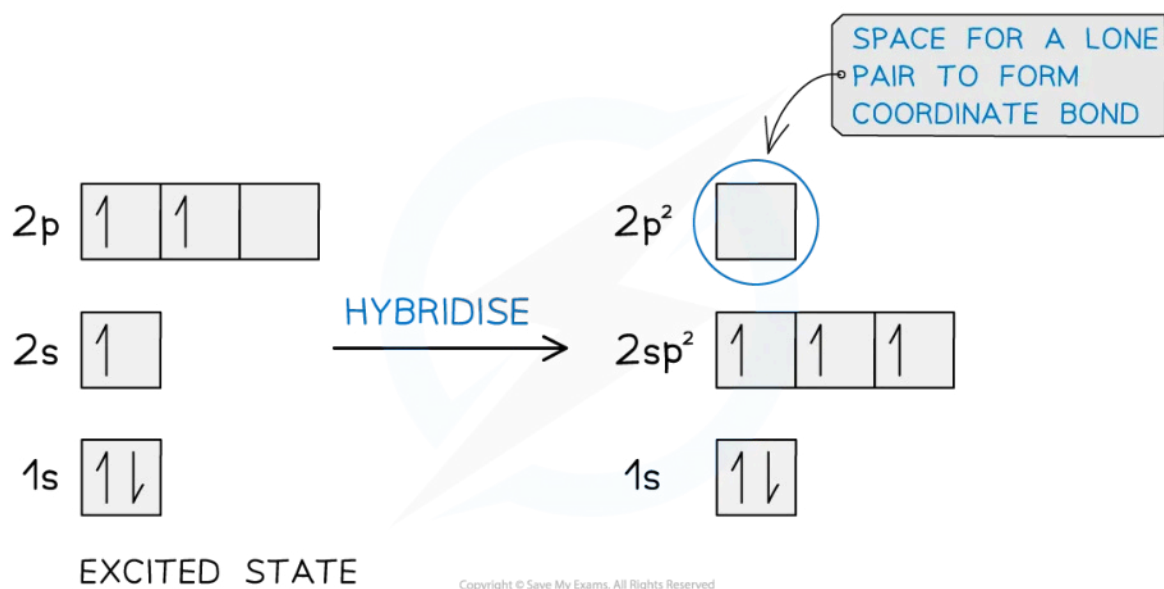
Hybridisation of the boron atom

Electrophiles and Nucleophiles

- An electrophile is an electron-deficient species that accepts a lone pair from another reactant to form a new covalent bond
  - An electrophile is therefore a Lewis acid
- A nucleophile is an electron-rich species that donates a lone pair to another reactant to form a new covalent bond
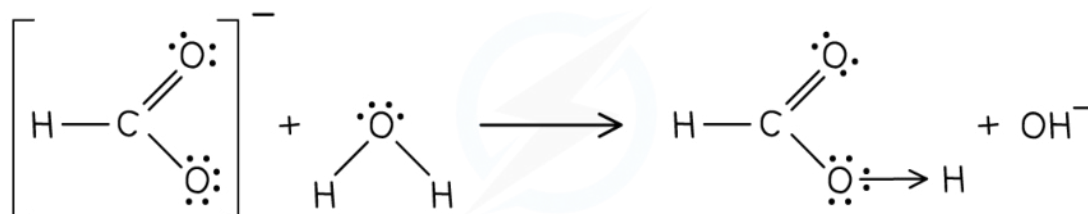 - A nucleophile is therefore a Lewis base
    Lewis acids behave as electrophiles and Lewis bases act as nucleophiles
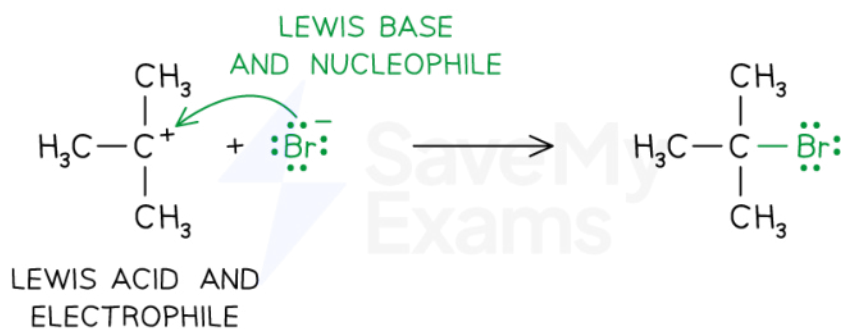
The carbocation, $C^+(CH_3)_3$ is accepting a pair of electrons from the bromide ion, Br^-

✏️ Worked example

Identify the Lewis acid and Lewis base in the following reaction

Answer

- The Lewis acid is water, H_2O
  - The hydrogen in the water molecule is accepting a pair of electrons leaving an OH^- ion
- The Lewis base is the methanoate ion, $HCOO^-$
  - The lone pair of electrons in the methanoate ion forms a coordinate bond with one of the hydrogens from the water molecule
  - We have seen previously that water can act as a Brønsted–Lowry acid or base, so it should be no surprise that water can act as both a Lewis acid or base depending on how it is interacting with other species

- Lewis acids and bases can also be seen in complex ions
- In the case of a complex ion, such as hexaaquacopper(II), the water molecule is acting as a Lewis base and the metal ion is acting as a Lewis acid
  - Copper(II), like other transition metals, can form a complex due to a partially occupied d subshell
  - Cu^{2+} (aq) $+ 6H_2O$ (l) $\rightarrow [Cu(H_2O)_6]^{2+}$ (aq)

Diagram showing the formation of the hexaaquacopper(II) complex
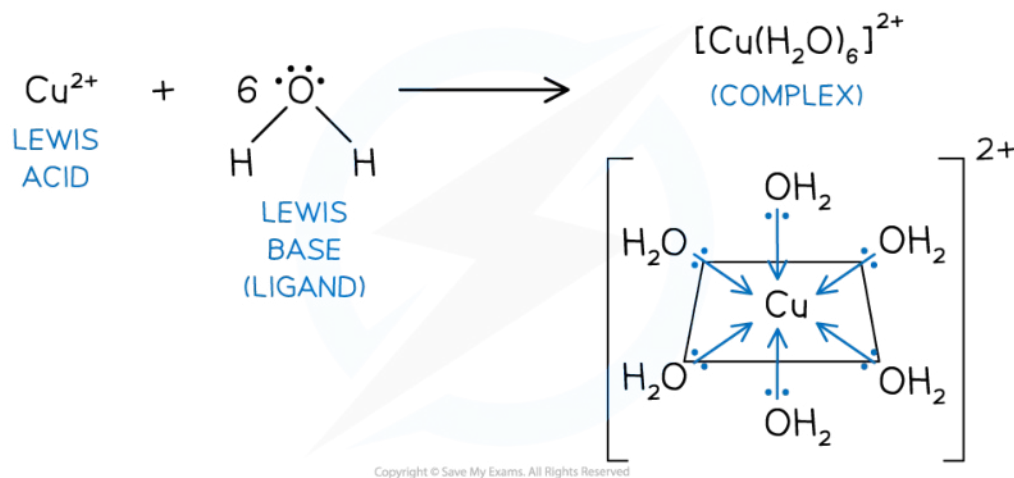
Hexaaquacopper(II) complex

- The Cu^{2+} ion acts as a Lewis acid and electrophile as it is accepting a lone pair of electrons from water
- The water molecules are acting as Lewis bases and nucleophiles as they are donating a lone pair of electrons to the Cu^{2+} ion
  - The cyanide ion, ^{-}CN and ammonia , NH_3 , are examples of Lewis bases and they can also act as nucleophiles

| Coordination Bonds (HL) | Your notes |

Coordination Bonds

- Transition element ions can form complexes which consist of a **central metal ion** and **ligands**
- A ligand is a molecule or ion that forms a co-ordinate bond with a transition metal by donating a pair of electrons to the bond
  - This is also the definition of a **Lewis base**
- This means ligands have a negative charge or a lone pair of electrons capable of being donated
  - This definition may seem familiar: a ligand is the same as a **nucleophile**
- Different **ligands** can form different numbers of coordination bonds to the central metal ion in a complex
  - **Monodentate** ligands can form **one** co-ordinate bond to the central metal ion
  - **Bidentate** ligands can form **two** co-ordinate bonds
  - **Multidentate** ligands can form **multiple** coordination bonds
- **Coordination number** is the number of co-ordinate bonds to the central metal atom or ion

Common Ligands

- Water molecules frequently act as ligands
- Each water molecule makes a single bond with the metal ion using one of the lone pairs on the oxygen atom
- The lone pair is donated to the partially filled d-subshell of the transition metal ion

### Table showing examples of common monodentate ligands

Name of Ligand	Formula of Ligand
Water	H_2O
Ammonia	NH_3
Chloride	Cl^-
Cyanide	CN^-
Hydroxide	OH^-

Representing complex ions

- Square brackets are used to group together the ligands and metal ion in a representation of the geometrical arrangement

- The overall charge on the complex ion is the sum of the oxidation states of all the species present
- If the ligands are neutral then the overall charge will be the same as the oxidation state of the metal ion

Examples of complexes with monodentate ligands
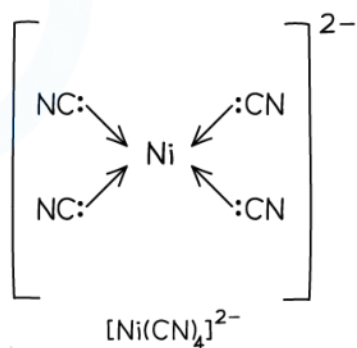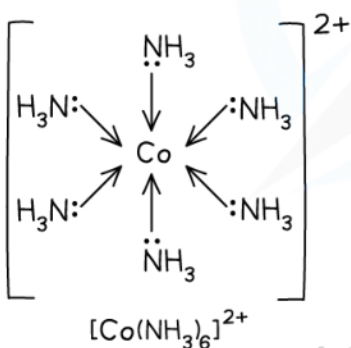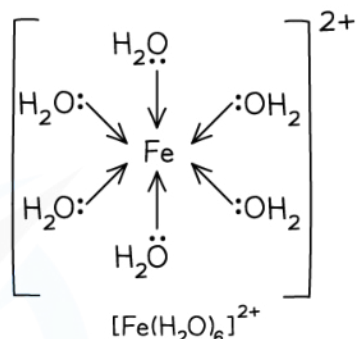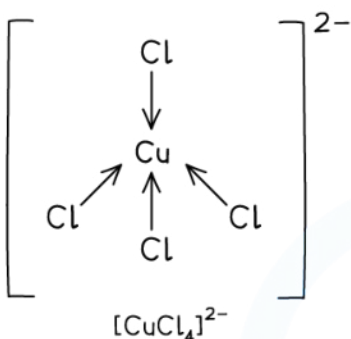
Each ligand has one lone pair of electrons so forms one coordinate bond to the central metal ion
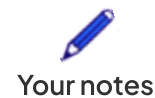
Coordination number

- The coordination number is the number of coordinate bonds to the metal ions
- This number can be the same as the number of ligands if they are monodentate
  - It can be different if bidentate or multidentate ligands are present
- Complexes with a coordination number of 4 commonly have a tetrahedral shape, while complexes with a coordination number of 6 have an octahedral shape

Charges of complex ions

- The charge of a complex ion depends upon three factors:
  - The charge of the central metal ion
  - The charge of the ligands
  - The coordination number
- If these factors are known then we can deduce the charge on the complex ion

Table showing the charges of complex ions

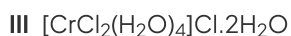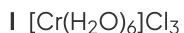| Central ion	Ligand	Coordination number	Charge on complex ion	Formula of complex ion
Cu^{2+}	Cl^-	4	$2^+ + (4 \times 1^-) = \mathbf{2^-}$	$[CuCl_4]^{2-}$
Fe^{2+}	H_2O	6	$2^+ + (6 \times 0) = \mathbf{2^+}$	$[Fe(H_2O)_6]^{2+}$
Fe^{3+}	H_2O	6	$3^+ + (6 \times 0) = \mathbf{3^+}$	$[Fe(H_2O)_6]^{3+}$
Ag^+	NH_3	2	$1^+ + (2 \times 0) = \mathbf{1^+}$	$[Ag(NH_3)_2]^+$

Your notes

Your notes

✏️ Worked example

The three formulas shown are compounds of chromium(III). What are the charges on the complex ions shown?

I $[Cr(H_2O)_6]Cl_3$

II $[CrCl(H_2O)_5]Cl_2.H_2O$

III $[CrCl_2(H_2O)_4]Cl.2H_2O$

A 0 , 0 , 0

B 1+, 2+, 3+

C 2+, 3+, 1+

D 3+, 2+, 1+

Answer:

- The correct option is **D**
- Water molecules do not contribute to the charge
- The chloride ion, Cl^-, outside the square brackets must balance against the charge on the complex
  - $[Cr(H_2O)_6]Cl_3$ contains three chloride ions
    - So, the charge on the complex is 3+
  - $[CrCl(H_2O)_5]Cl_2.H_2O$ contains two chloride ions outside the square bracket
    - So, the charge on the complex is 2+
  - $[CrCl_2(H_2O)_4]Cl.2H_2O$ contains one chloride ion outside the square bracket
    - So, the charge on the complex is 1+

Bidentate ligands

- **Bidentate** ligands can each form **two** co-ordinate bonds to the central metal ion
- This is because each ligand contains **two** atoms with lone pairs of electrons
- Examples of bidentate ligands are:
  - 1,2–diaminoethane ($H_2NCH_2CH_2NH_2$) which is also written as **'en'**
  - Ethanedioate ion ($C_2O_4^{2-}$) which is sometimes written as **'ox'** (coming from the common name of oxalate)

Transition metal complexes with bidentate ligands diagram

Your notes


$[Cu(en)_3]^{2+}$ $[Co(C_2O_4)_3]^{3-}$
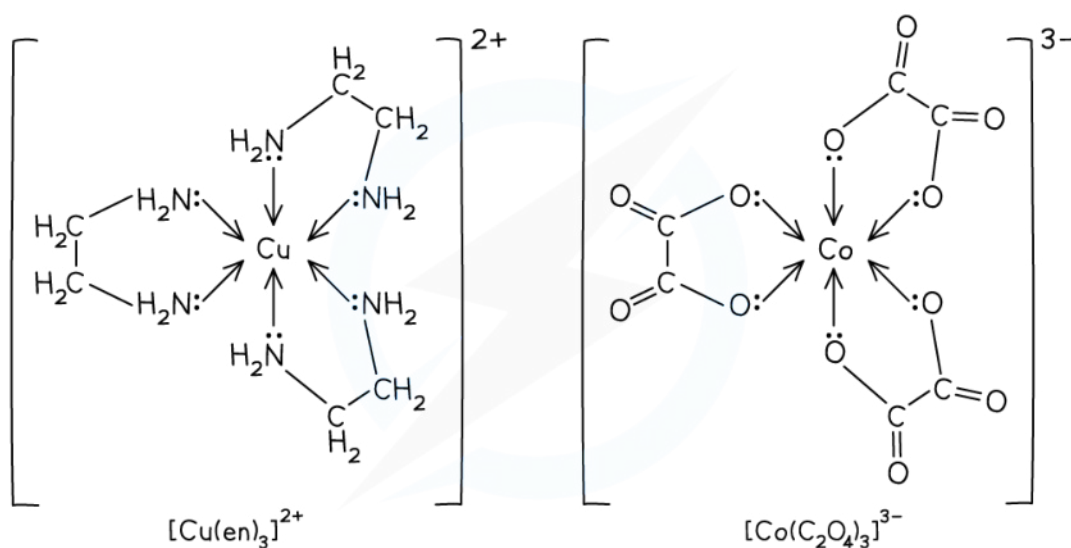
Each ligand has two lone pairs of electrons so forms two coordinate bonds to the central metal ion

Multidentate ligands

- Some ligands contain more than two atoms with lone pairs of electrons
- These ligands can form more than two dative bonds and are said to be **multidentate** or **polydentate** ligands
- An example of a multidentate ligand is EDTA^{4-}, which is a **hexadentate** ligand as it forms 6 dative covalent bonds to the central metal ion
- EDTA comes from **e**thylene**d**iamine**t**etra**a**cetic acid, which is rather a mouthful so EDTA is easier!

Transition metal complexes with multidentate ligands diagram

EDTA LIGAND Cu^{2+} COPPER (II) – EDTA COMPLEX
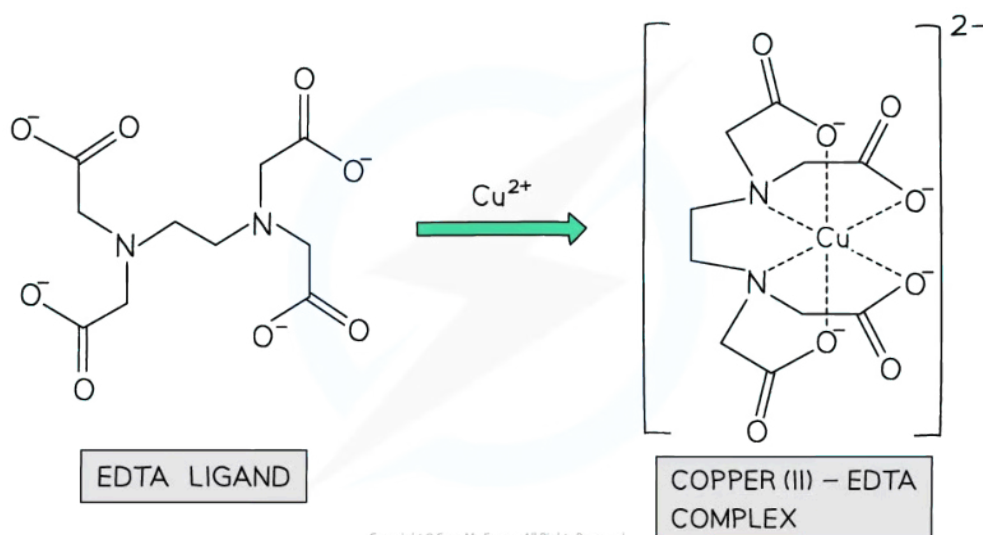
The ligands contain more than one atom with a lone pair of electrons so multiple coordinate bonds are formed

Your notes

Nucleophilic Substitution in Halogenoalkanes (HL)

Nucleophilic Substitution in Halogenoalkanes

- In nucleophilic substitution reactions involving halogenoalkanes, the halogen atom is replaced by a nucleophile
- The strength of any nucleophile depends on its ability to make its lone pair of electrons available for reaction
- The hydroxide ion, OH^-, is a stronger nucleophile than water because it has a full negative charge
  - This means that it has a readily available lone pair of electrons

- A water molecule only has partial charges, $\delta+$ and $\delta-$
  - This means that its lone pair of electrons is less available than the hydroxide ions
  - The lone pairs of electrons in a water molecule are still available to react

Lewis diagram of OH^- and H_2O

Lewis formulae of the hydroxide ion and water molecule – illustrating the lone pairs of electrons and charges within their structures

> **Examiner Tip**
>
> - In general:
>   - A negatively charged ion will be a stronger nucleophile than a neutral molecule
>   - A conjugate base will be a stronger nucleophile than its corresponding conjugate acid
>   - e.g. the hydroxide ion is a stronger nucleophile than water

- Nucleophilic substitution reactions can occur in two different ways (known as S_N2 and S_N1 reactions) depending on the structure of the halogenoalkane involved

S_N1 reactions

- In **tertiary** halogenoalkanes, the carbon that is attached to the halogen is also bonded to three alkyl groups
- These halogenoalkanes undergo nucleophilic substitution by an S_N1 mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '1' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of only one reagent, the halogenoalkane

Meaning of S_N1
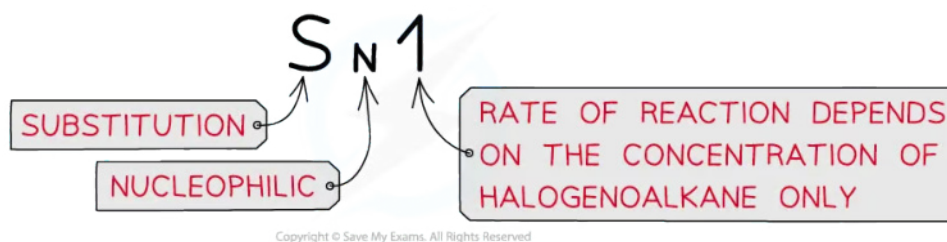
'S' stands for substitution, N stands for nucleophilic and '1' shows that the rate of reaction depends upon the concentration of one reagent

- The S_N1 mechanism is a **two-step** reaction
- In the first step, the C-X bond breaks heterolytically and the halogen leaves the halogenoalkane as an X^- ion (this is the **slow** and **rate-determining step**)
  - As the rate-determining step only depends on the concentration of the halogenoalkane, the rate equation for an S_N1 reaction is **rate = k[halogenoalkane]**
  - In terms of molecularity, an S_N1 reaction is unimolecular
  - This forms a tertiary carbocation intermediate (which is a tertiary carbon atom with a positive charge)
  - In the second step, the tertiary carbocation is attacked by the nucleophile
- This two-step process is evident in the energy profile diagram for an S_N1 reaction
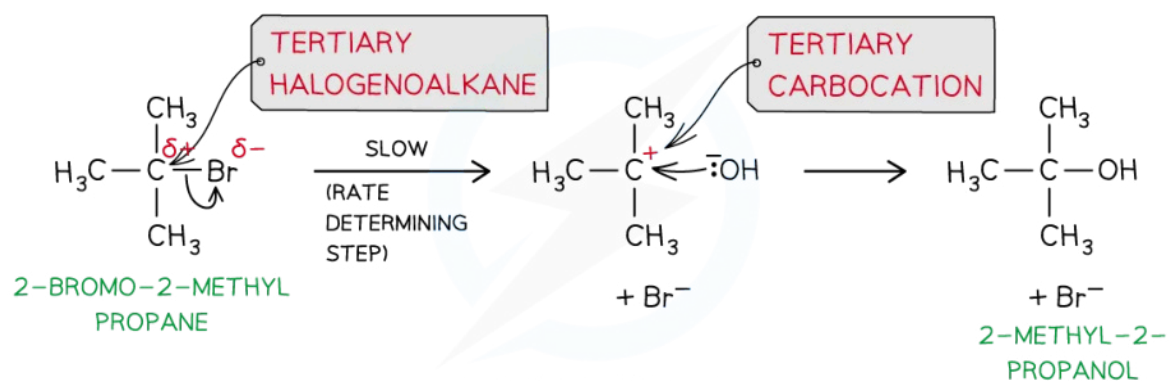
Reaction profile for an S_N1 mechanism
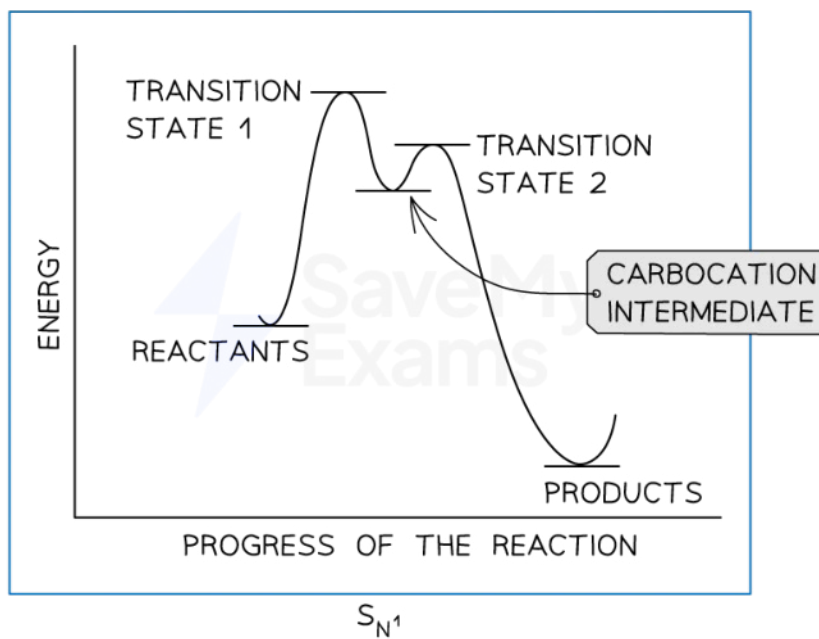
Your notes

The reaction profile for an S$_N$1 mechanism is a two-step mechanism so has two curves. The connection between the first two curves represents the carbocation intermediate

- For example, the nucleophilic substitution of 2-bromo-2-methylpropane by hydroxide ions to form 2-methyl-2-propanol

Example of S$_N$1 mechanism

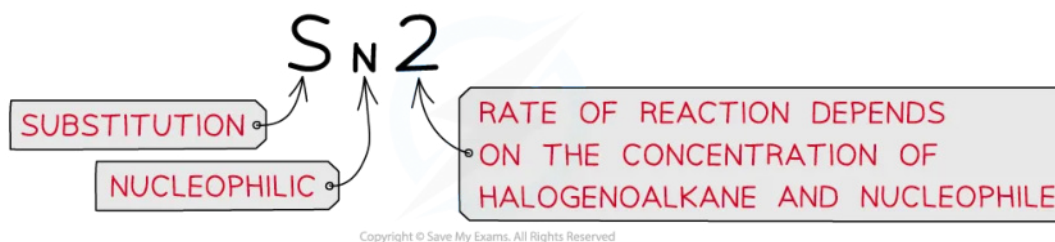*The mechanism of nucleophilic substitution in 2-bromo-2-methylpropane which is a tertiary halogenoalkane*


💡 **Examiner Tip**

- You are expected to know the difference between the heterolytic fission that features in S$_N$1 reactions and homolytic fission in other reactions:
  - Heterolytic fission forms anions and cations and uses double-headed arrows to show the movement of both electrons from the covalent bond
  - Homolytic fission forms free radicals and uses single-headed arrows, sometimes called fish hooks, to show the movement of a single electron as the covalent bond breaks

---

S$_N$2 reactions

- In **primary** halogenoalkanes, the carbon that is attached to the halogen is bonded to one alkyl group
  - These halogenoalkanes undergo nucleophilic substitution by an **S$_N$2** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '2' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of both the halogenoalkane and the nucleophile ions

Meaning of S$_N$2
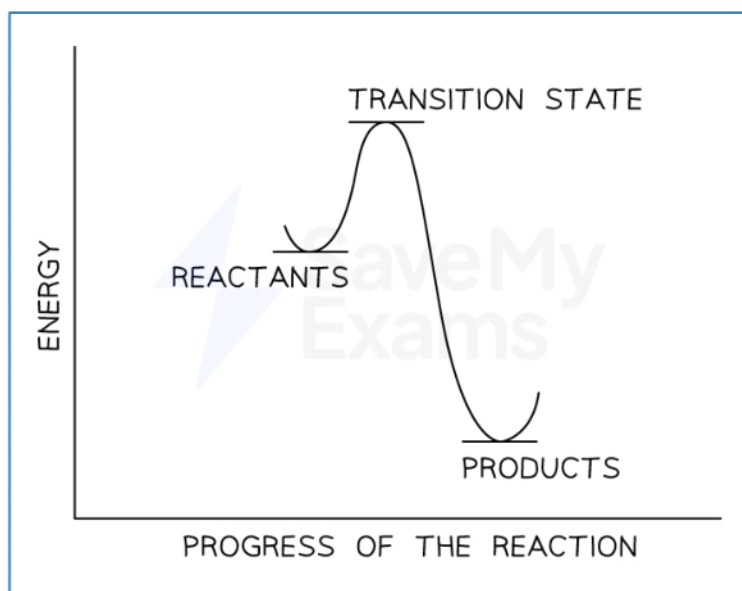
Copyright © Save My Exams. All Rights Reserved
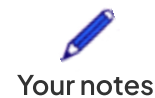
'S' stands for substitution, N stands for nucleophilic and '2' shows that the rate of reaction depends upon the concentration of both the halogenoalkane and the nucleophile ions

- The S_N2 mechanism is a **one-step** reaction
  - The nucleophile donates a pair of electrons to the δ+ carbon atom of the halogenoalkane to form a new bond
  - As this is a one-step reaction, the rate-determining step depends on the concentrations of the halogenoalkane and nucleophile which means that the rate equation for an S_N2 reaction is

  rate = *k*[halogenoalkane][nucleophile]

  - In terms of molecularity, an S_N2 reaction is bimolecular
  - At the same time, the C-X bond is breaking and the halogen (X) takes both electrons in the bond (heterolytic fission)
  - The halogen leaves the halogenoalkane as an X^- ion
- This one-step process is evident in the energy profile diagram for an S_N2 reaction
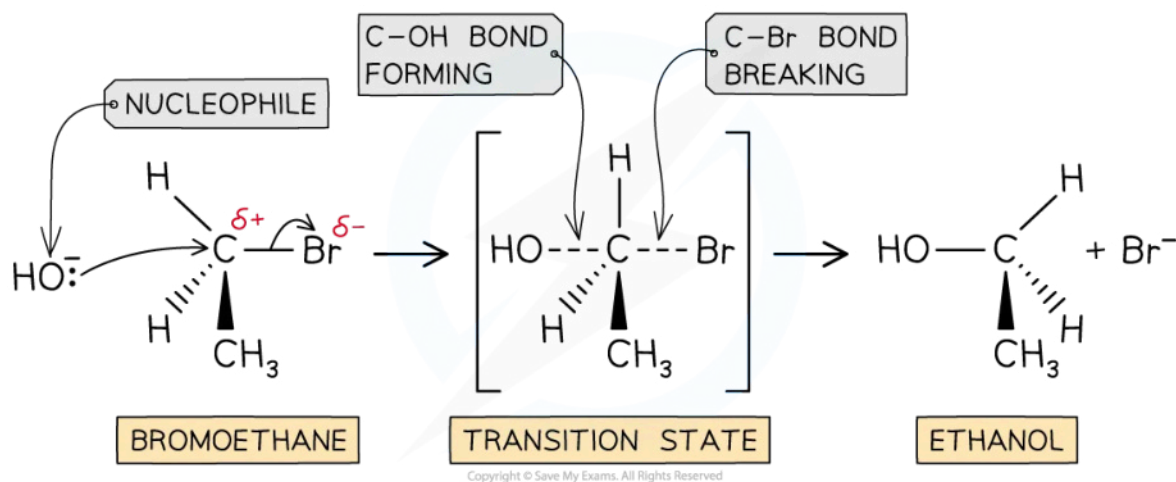
Reaction profile for an S_N2 mechanism

The reaction profile for an S_N2 mechanism is a one-step reaction so has one curve. The transition state always involves partial bonds

- For example, the nucleophilic substitution of bromoethane by hydroxide ions to form ethanol

Example of an S_N2 mechanism

The S_N2 mechanism of bromoethane with hydroxide causes an inversion of configuration

- The bromine atom of the bromoethane molecule causes **steric hindrance**
- This means that the hydroxide ion nucleophile can only attack from the opposite side of the C-Br bond

- An attack from the same side as the bromine atom is sometimes called a frontal attack
    - While attack from the opposite side is sometimes called a backside or rear-side attack
- As a result of this, the molecule has undergone an inversion of configuration
- The common comparison for this is an umbrella turning inside out in the wind
- As the C-OH bond forms, the C-Br bond breaks causing the bromine atom to leave as a bromide ion

Diagram to demonstrate inversion of configuration
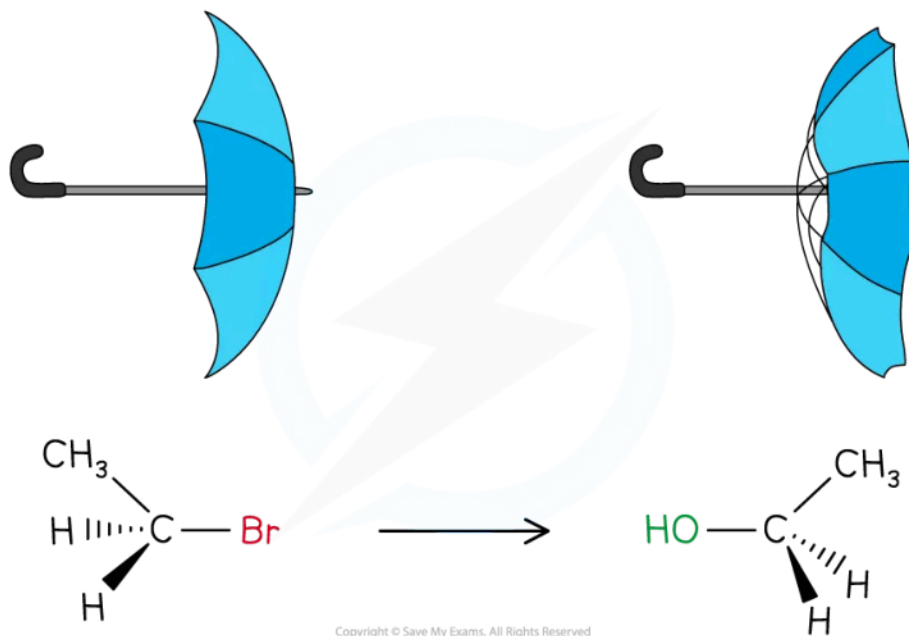
Inversion of configuration – umbrella analogy

💡 Examiner Tip

- If you are asked to explain reaction mechanisms where there is an inversion of configuration, you will be expected to:
    - Use partial charges, δ+ and δ-, to help explain why the nucleophile attacks and the halogen leaves
    - Use dotted, wedge and tapered bonds to show the change in configuration of the atoms / functional groups around the carbon that is being attacked
    - Draw the transition state with the nucleophile attached to the carbon with a dotted bond and the halogen still attached to the carbon, also, with a dotted bond
    - Be aware that the compound you draw is a transition state and not an intermediate

Relative Rates of Nucleophilic Substitution (HL)

Your notes

Relative Rates of Nucelophilic Substitution

- Various factors affect the rate of nucleophilic substitution, regardless of S_N1 or S_N2, involving a halogenoalkane:
    1. The nature of the nucleophile
    2. The halogen involved (leaving group)
    3. The structure (class) of the halogenoalkane

1. The nature of the nucleophile

- The most effective nucleophiles are neutral or negatively charged species that have a lone pair of electrons available to donate to the δ+ carbon in the halogenoalkane
- The greater the electron density on the nucleophile ion or molecule; the stronger the nucleophile
    - Consequently, negative anions tend to be more reactive than their corresponding neutral species, e.g. hydroxide ions and water molecules (as previously discussed)
- When nucleophiles have the same charge, the electronegativity of the atom carrying the lone pair becomes the deciding factor
    - The less electronegative the atom carrying the lone pair; the stronger the nucleophile
    - For example, ammonia is a stronger electrophile than water because the nitrogen atom in ammonia is less electronegative than the oxygen atom in water
        - This is because a less electronegative atom has a weaker grip on its lone pair of electrons, which means that they are more available for reaction
- The effectiveness of nucleophiles is as follows:

Strongest $CN^- > OH^- > NH_3 > H_2O$ Weakest

2. The halogen involved (leaving group)

- The halogenoalkanes have different rates of substitution reactions
- Since substitution reactions involve breaking the carbon-halogen bond, the bond energies can be used to explain their different reactivities

Approximate Halogenoalkane Bond Energy Table

Bond	Bond Energy / kJ mol^{-1}
C–F	492 (strongest bond)
C–Cl	324
C–Br	285
C–I	228 (weakest bond)

- The table above shows that the C–I bond requires the least energy to break, i.e. it is the weakest carbon-halogen bond
  - During substitution reactions, the C–I bond will break heterolytically as follows:

$$R_3C-I + OH^- \rightarrow R_3C-OH + I^-$$

- The C–F bond, on the other hand, requires the most energy to break and is, therefore, the strongest carbon-halogen bond
  - Fluoroalkanes will therefore be less likely to undergo substitution reactions

- This idea can be confirmed by reacting the product formed by nucleophilic substitution of the halogenoalkane with an aqueous silver nitrate solution
- As a halide ion is released, this results in the formation of a precipitate
- The rate of formation of these precipitates can also be used to determine the reactivity of the halogenoalkanes
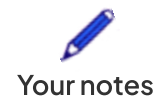
Halogenoalkane Precipitates Table

Halogenoalkane	Precipitate
Chloride	White (silver chloride)
Bromide	Cream (silver bromide)
Iodide	Pale yellow (silver iodide)

- The formation of the pale yellow silver iodide is the fastest (fastest nucleophilic substitution reaction) whereas the formation of the silver fluoride is the slowest (slowest nucleophilic substitution reaction)
- This confirms that fluoroalkanes are the least reactive and iodoalkanes are the most reactive halogenoalkanes

### Diagram to show the relative reactivity of the halogenoalkanes

Your notes

FLUOROALKANES

CHLOROALKANES

BROMOALKANES

IODOALKANES

LEAST REACTIVE

MOST REACTIVE
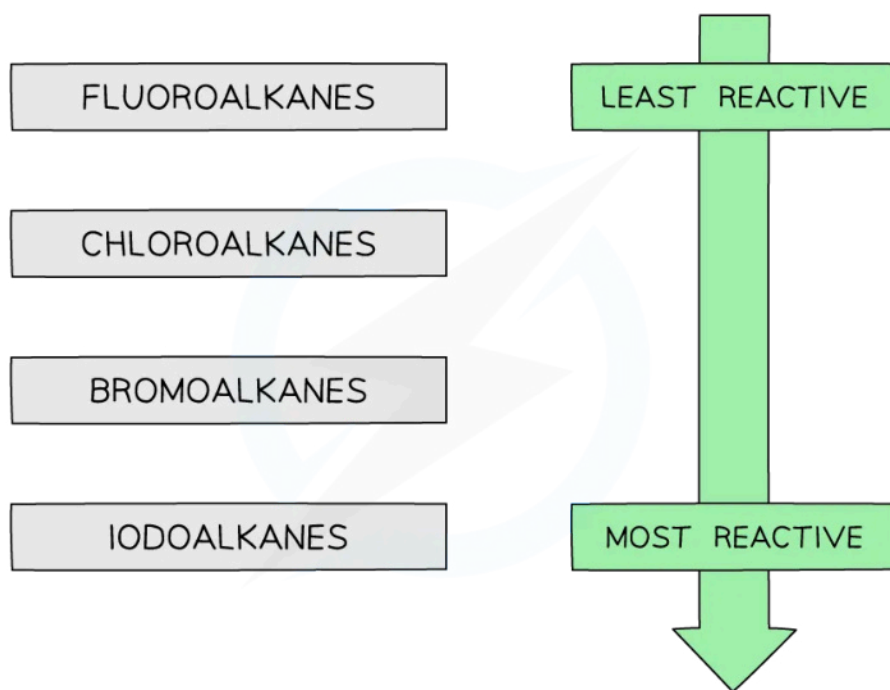
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The trend in reactivity of halogenoalkanes

3. The structure (class) of the halogenoalkane

- Tertiary halogenoalkanes undergo S_N1 reactions, forming stable tertiary carbocations
- Secondary halogenoalkanes undergo a mixture of both S_N1 and S_N2 reactions depending on their structure
- Primary halogenoalkanes undergo S_N2 reactions, forming the less stable primary carbocations
- This has to do with the **positive inductive effect** of the alkyl groups attached to the carbon which is bonded to the halogen atom
  - The alkyl groups push electron density towards the positively charged carbon, reducing the charge density
  - In tertiary carbocations, there are three alkyl groups stabilising the carbocation
  - In primary carbocations, there is only one alkyl group
    - This is why tertiary carbocations are much more stable than primary ones

Primary, secondary and tertiary carbocations
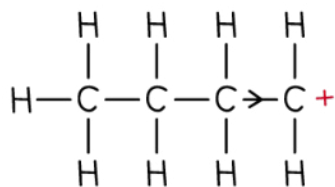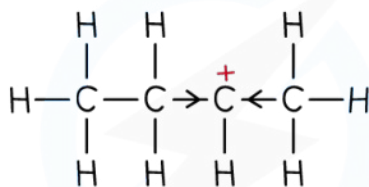
Your notes
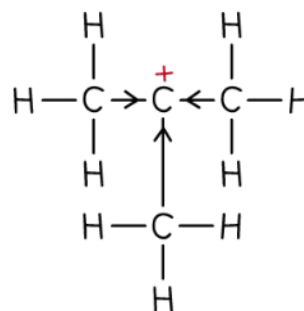
The diagram shows the trend in the stability of primary, secondary and tertiary carbocations

- Overall, the structure (class) has a direct effect on the formation of the carbocation and, therefore, the rate-determining step
- Consequently, this affects the overall rate of the nucleophilic substitution reaction

The Mechanisms of Electrophilic Addition Reactions (HL)

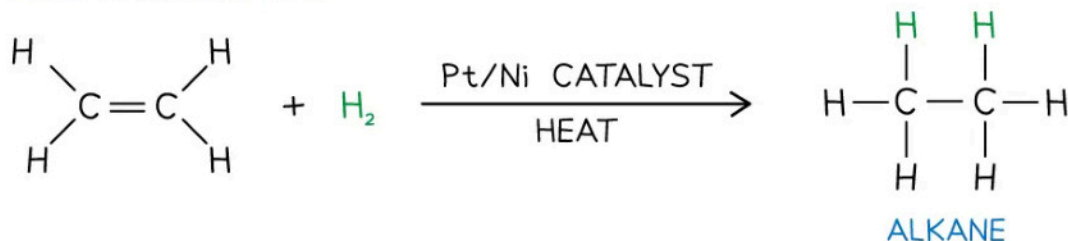## The Mechanisms of Electrophilic Addition Reactions

Electrophilic Addition

- **Electrophilic addition** is the addition of an electrophile (or Lewis acid) to an alkene double bond, C=C
- The alkene double bond, C=C, is an area of high electron density which makes it susceptible to attack by electrophiles
- The C=C bond breaks forming a single C–C bond and 2 new bonds from each of the two carbon atoms
- Electrophilic addition reactions include the addition of:
    - Hydrogen, H_2 (g)
    - Steam, H_2O (g)
    - Hydrogen halides, HX
    - Halogens, X_2

Different reactions of the alkenes including reagents and conditions
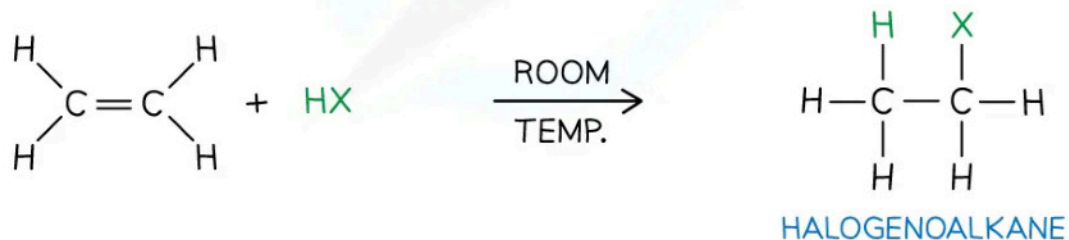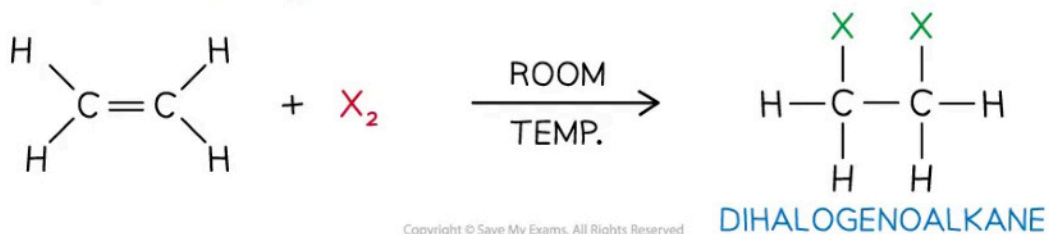
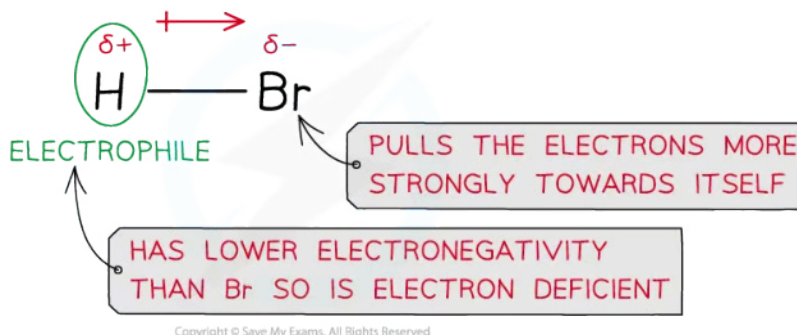*Alkene electrophilic addition reaction overview*

Addition of hydrogen halides

- A hydrogen halide molecule is polar as the hydrogen and halogen atoms have different electronegativities

- For example, in a molecule of hydrogen bromide, HBr, the bromine atom has a stronger pull on the electrons in the H-Br bond
- As a result of this, the Br atom has a partial negative charge and the H atom a partial positive charge

Partial charges in the H–Br bond

Due to differences in electronegativities of the hydrogen and bromine atom, HBr is a polar molecule

- In electrophilic addition reactions with hydrogen halides, the H atom acts as an electrophile and Lewis acid by accepting a pair of electrons from the C=C bond in the alkene
  - The H-Br bond breaks heterolytically, forming a Br^- ion

- This results in the formation of a highly reactive carbocation intermediate which reacts with the bromide ion, Br^-
- For example, the mechanism for the electrophilic addition of hydrogen bromide and ethene is:

Electrophilic addition mechanism
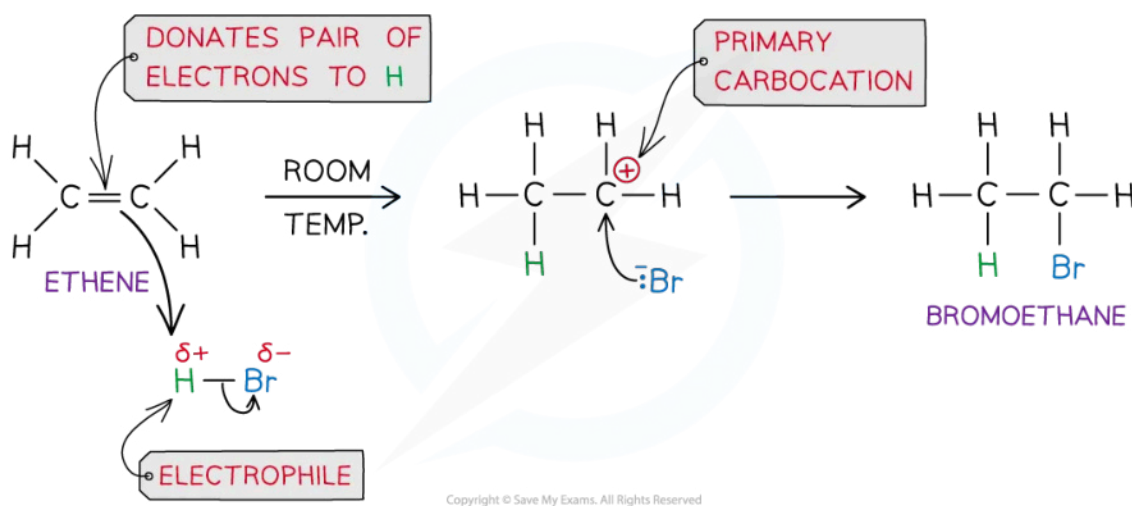
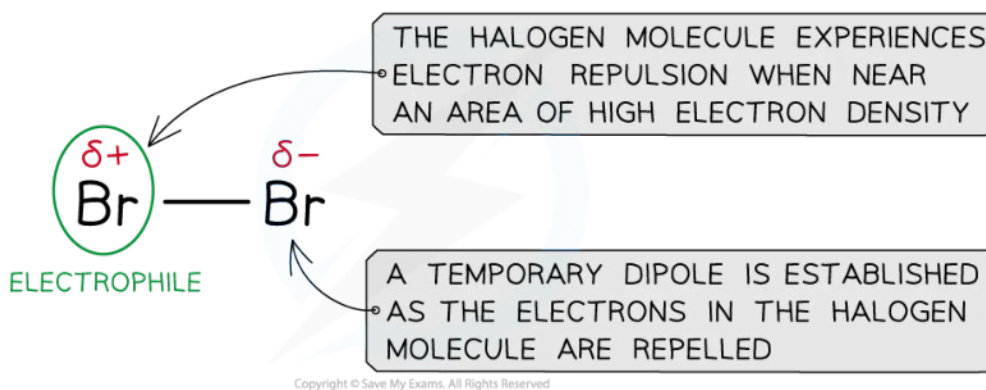*Electrophilic addition reaction of HBr and ethene to form bromoethane*
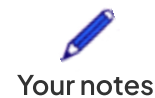
> 💡 **Examiner Tip**
>
> - For electrophilic addition mechanisms, the curly arrows must:
>   - Be double-headed to show the movement of a pair of electrons
>   - Start from a lone pair of electrons or an area of high electron density, e.g. the C=C bond
>   - Move towards a δ+ electrophile or the positive charge of a carbocation
>
> - Examiners often comment about the poor and incorrect use of curly arrows in organic mechanisms

Addition of halogens

- The mechanism for the electrophilic addition of halogens (and hydrogen) is the same as the electrophilic addition of hydrogen halides with one key exception:
- Hydrogen halide molecules have a **permanent dipole** (as shown above)
- Halogen molecules have a **temporary (or induced) dipole** caused by the repulsion of the halogens electrons by the high electron density C=C bond

The partial charges in a halogen molecule are caused by the high electron density in the C=C bond

The temporary (or induced) dipole in a halogen molecule

> 💡 **Examiner Tip**
>
> - The electrophilic addition reactions of alkenes with hydrogen halides and halogens are the same
> - The difference is whether the electrophile is due to a permanent or temporary dipole

Addition of water

- Water is a weak electrophile, so does not undergo addition reactions with alkenes unless in the presence of a strong acid which can act as a catalyst
  - H_3O^+ acts as the electrophile

Your notes

- The reaction occurs in two steps
  - Step 1
    - The π electrons in the C=C are attracted to H3O+
    - Heterolytic fission occurs and a carbocation is formed
  - Step 2
  - Water acts as a nucleophile and donates a pair of electrons to the positive carbon atom forming the C-O bond
  - An equilibrium is established between the positive product and the deprotonated product (the alcohol)
  - The H_3O^+ is regenerated as the catalyst

Electrophilic addition of water

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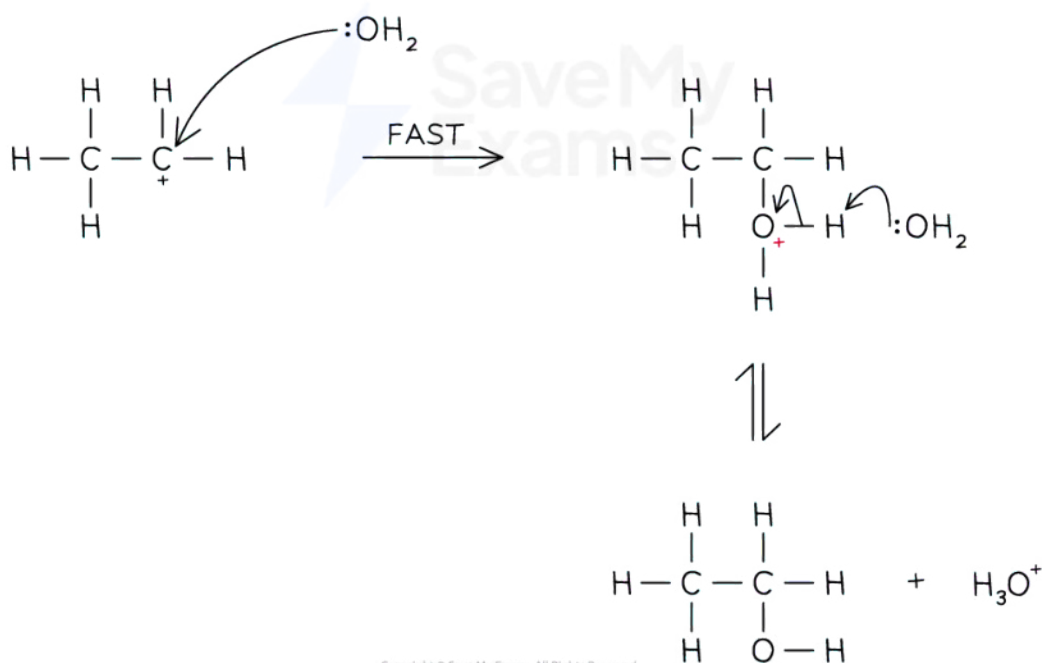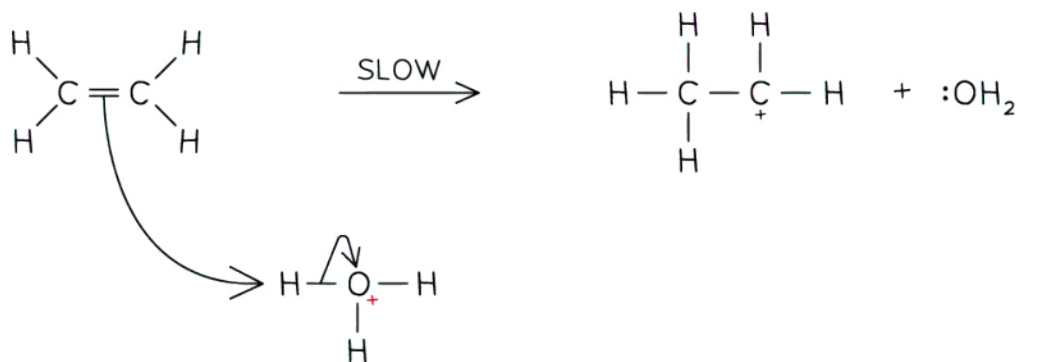
This mechanism is catalysed by concentrated acid

Addition to Unsymmetrical Alkenes (HL)

Addition to Unsymmetrical Alkenes

- **Carbocations** are positively charged carbon atoms with only three covalent bonds instead of four
- There are three types of carbocations: primary, secondary and tertiary

Inductive effect

- The alkyl groups attached to the positively charged carbon atoms are 'electron donating groups'
  - This is also known as the inductive effect of alkyl groups
- The inductive effect is illustrated by the use of arrowheads on the bonds to show the alkyl groups pushing electrons towards the positively charged carbon
  - This causes the carbocation to become less positively charged
- As a result of this, the charge is spread around the carbocation which makes it energetically more stable
- This means that tertiary carbocations are the most stable as they have three electron-donating alkyl groups which energetically stabilise the carbocation
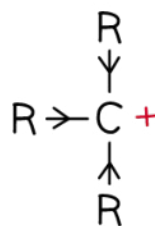- Due to the positive charge on the carbon atom, carbocations are electrophiles

Primary, secondary and tertiary carbocations
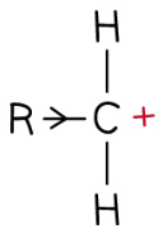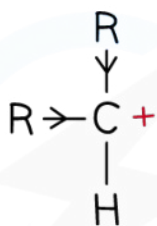
Alkyl groups push electron density towards the carbocation making it energetically more stable; the more alkyl groups the carbocation is bonded to, the more stabilised it is

Markovnikov's rule

- Markovnikov's rule predicts the outcome of electrophilic addition reactions and states that:
  - In an electrophilic addition reaction of a hydrogen halide (HX) to an alkene, the halogen ends up bonded to the most substituted carbon atom
  - In an electrophilic addition reaction of an interhalogen to an alkene, the most electronegative halogen ends up bonded to the most substituted carbon atom
- Markovnikov addition applies to electrophilic addition reactions with unsymmetrical alkanes, e.g. propene and but-1-ene

- Markovnikov addition favours the formation of the major product
- Anti-Markovnikov addition favours the formation of the minor product

- In electrophilic addition reactions, an electrophile reacts with the double bond of alkenes (as previously discussed)
- The mechanism for electrophilic addition reactions with unsymmetrical alkenes is slightly different, e.g. propene + hydrogen bromide

### Step 1 in the electrophilic addition mechanism
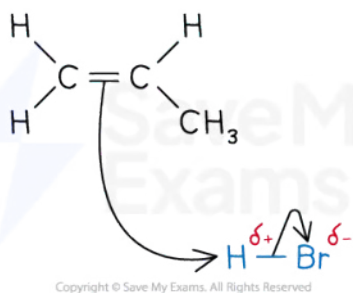
The electrophile reacts with the electron-rich C–C double bond

- The electrophile can attach in two possible ways:
  1. Breaking the C=C bond and attaching to the least substituted carbon
     - This will give the **most** stable carbocation as an intermediate that will form the **major** product
  2. Breaking the C=C bond and attaching to the most substituted carbon
     - This will give the **least** stable carbocation as an intermediate that will form the **minor** product

Relative stabilities of primary and secondary carbocations
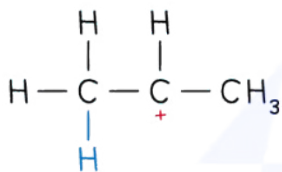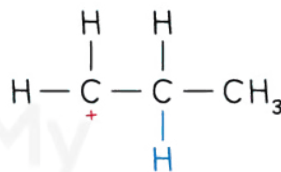
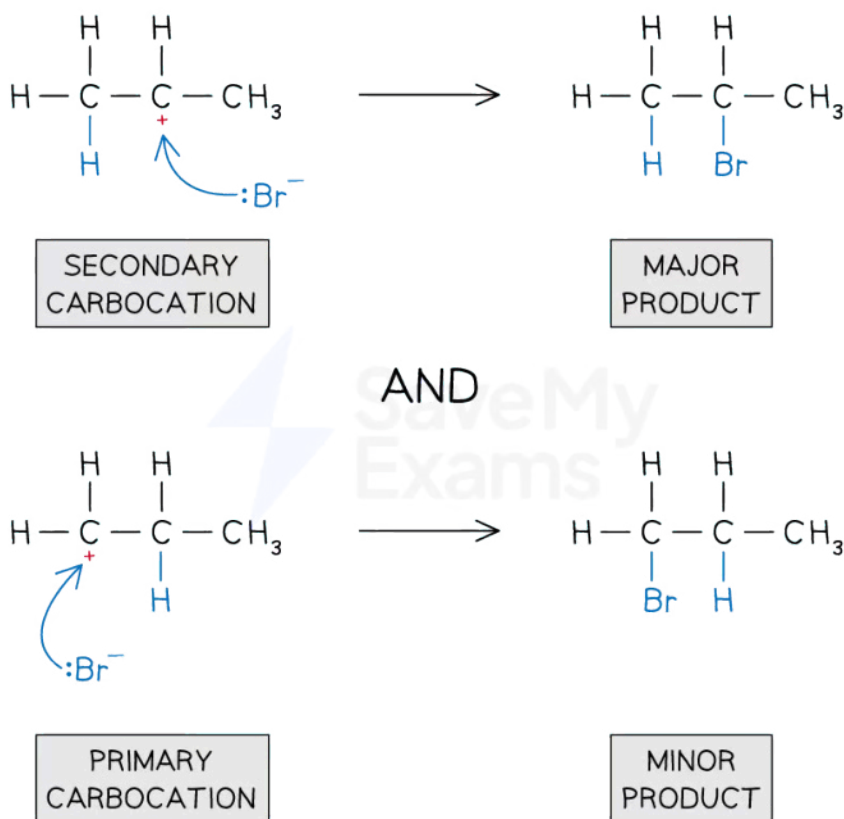*The major and minor carbocation intermediates formed during the reaction of propene and hydrogen bromide*

- The nucleophile will bond to the positive carbon atom of the carbocation
- The more stable carbocation produces the major product
- The less stable carbocation produces the minor product

### Formation of major and minor products

Your notes

Formation of the major and minor products of the reaction of propene with hydrogen bromide

- The mechanism for the electrophilic addition of hydrogen bromide to propene, showing the formation of the major and minor products can be shown as:

Electrophilic addition mechanism showing the formation of the major and minor products

Your notes
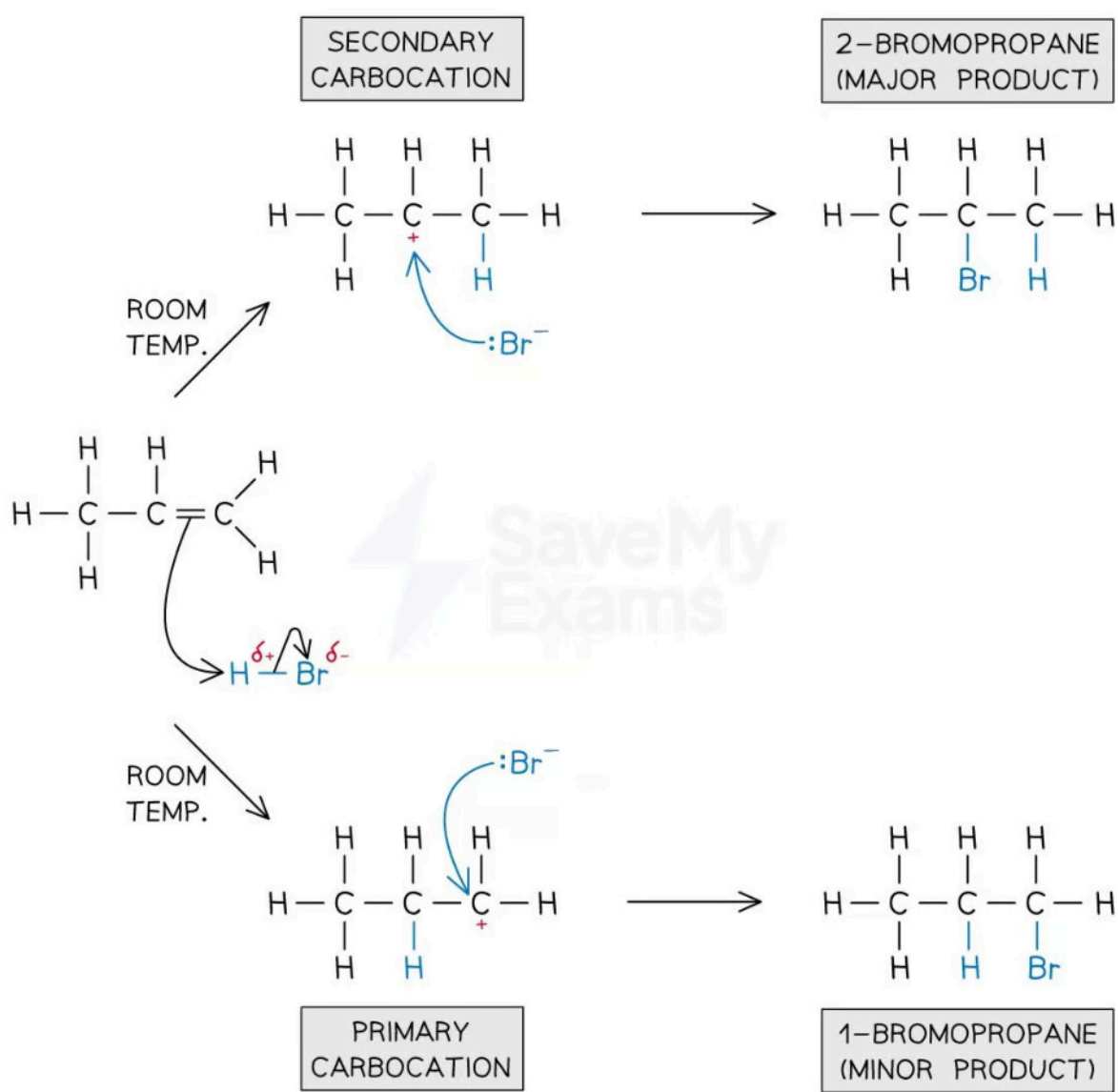
The electrophilic addition reaction mechanism of HBr and propene to form 1-bromopropane and 2-bromopropane

💡 Examiner Tip

- The stability of the carbocation intermediate is as follows:

  tertiary > secondary > primary

- When more than one carbocation can be formed, the major product of the reaction will be the one that results from the nucleophilic attack of the most stable carbocation.
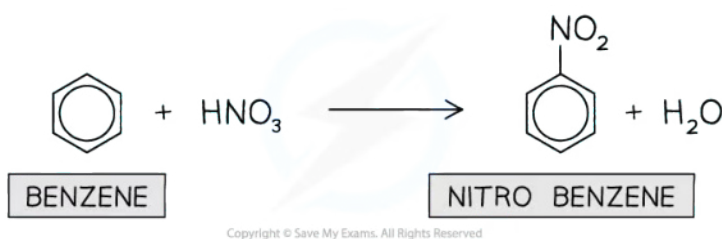
Electrophilic Substitution in Benzene (HL)

Electrophilic Substitution in Benzene

Reactions of Benzene

- Benzene undergoes a wide range of reactions including combustion - (complete and incomplete) and nitration
- Nitration involves the substitution of a hydrogen atom from the benzene ring with an electrophilic atom or group of atoms

Nitration of benzene

In nitration reactions, a nitro (–NO$_2$) group replaces a hydrogen atom on the arene

- Nitration is an **electrophilic substitution** reaction
  - This is different to the reactions of unsaturated alkenes, which involve the double bond breaking and the **electrophile** atoms 'adding across' the carbon atoms

Electrophilic substitution reaction

- The **electrophilic substitution** reaction in arenes consists of **three steps**:
  1. Generation of an **electrophile**
  2. **Electrophilic attack**
  3. Regenerating **aromaticity**

Generation of an electrophile

- The **delocalised π system** is extremely stable and is a region of **high electron density**
- Consequently, the **first step** of an electrophilic substitution reaction involves the generation of an electrophile
  - An electrophile can be a positive ion or the positive end of a polar molecule
- The electrophile for nitration is the nitronium ion, NO_2^+
  - This is produced **in situ**, by adding a mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4), at a temperature between 25 and 60 $^\circ$C, to the reaction mixture
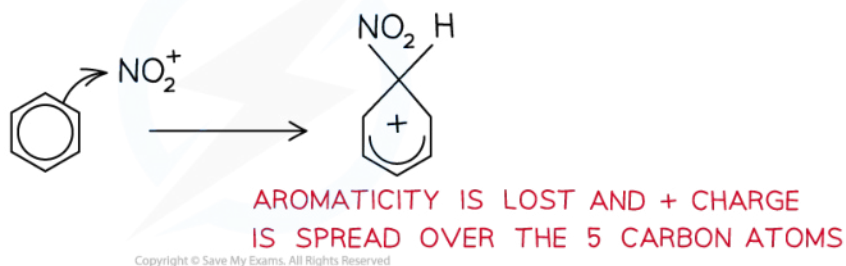
Electrophilic attack

- The **second step** in nitration is when a pair of electrons from the benzene ring is donated to the electrophile to form a **covalent bond**

- This disrupts the aromaticity in the ring as there are now only four π electrons and there is a **positive charge** spread over the five carbon atoms

The electrophilic attack of the nitronium ion by benzene

Electrons from the benzene π bonding system attack the electrophile

Regenerating aromaticity

- In the **third step** of electrophilic substitution, the aromaticity of the benzene ring system is restored
- This happens by **heterolytic cleavage** of the C-H bond
  - This means that the electrons in this bond go into the benzene π bonding system

Breaking a C-H bond to restore aromaticity

The C-H bond breaks heterolytically to restore the aromaticity of the benzene π bonding system