SL IB Chemistry

Your notes

Electron Pair Sharing Reactions

Contents

Nucleophilic Substitution

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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

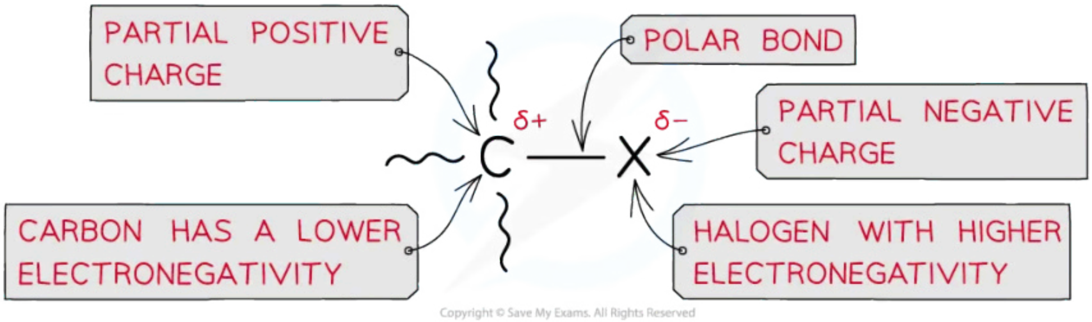
Neutral	Charged
H_2O	OH^-
NH_3	Cl^-
ROH	CN^-
RNH_2	R^- (carbanions)

- 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



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

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, δ+, 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:

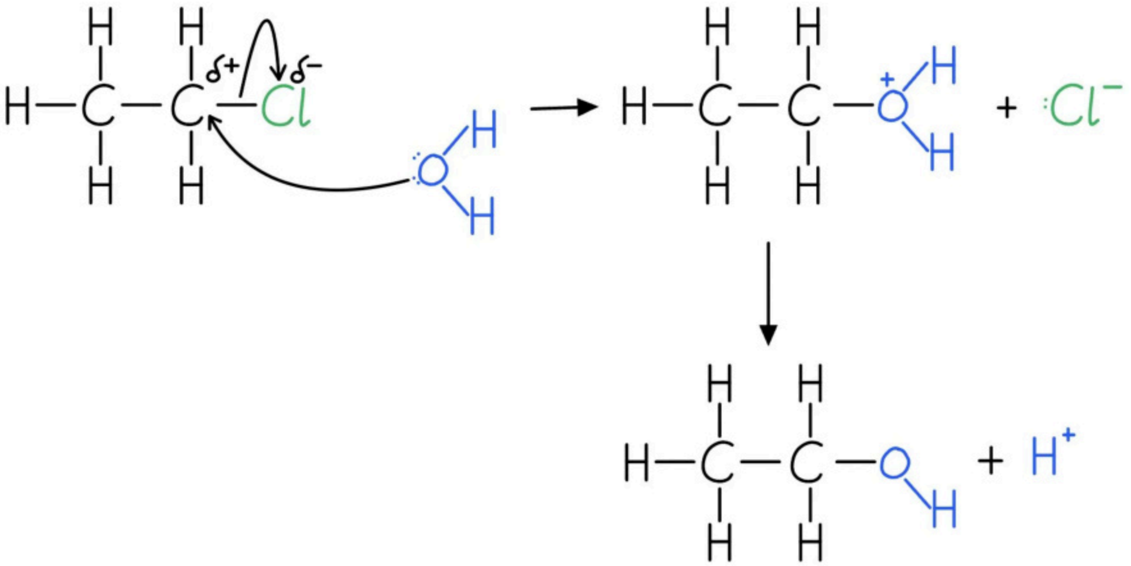
Nucleophilic substitution mechanism of bromoethane with a hydroxide ion

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

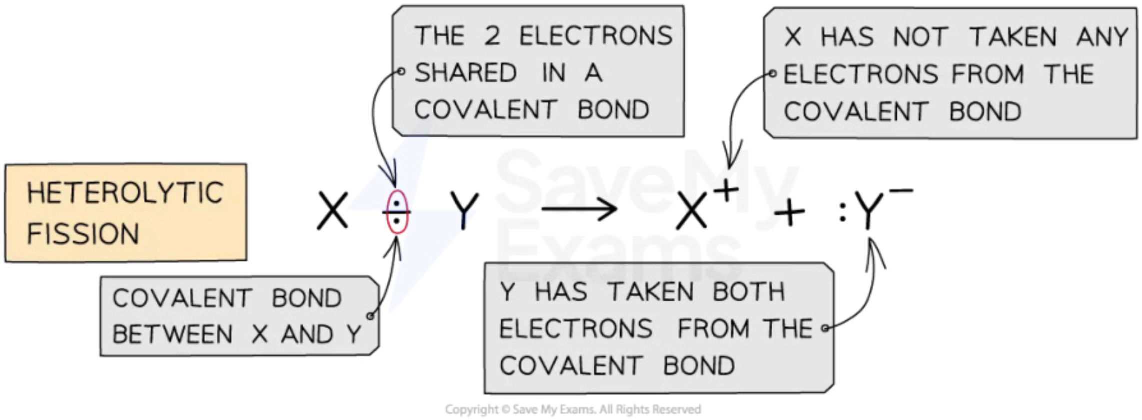
Heterolytic Fission

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

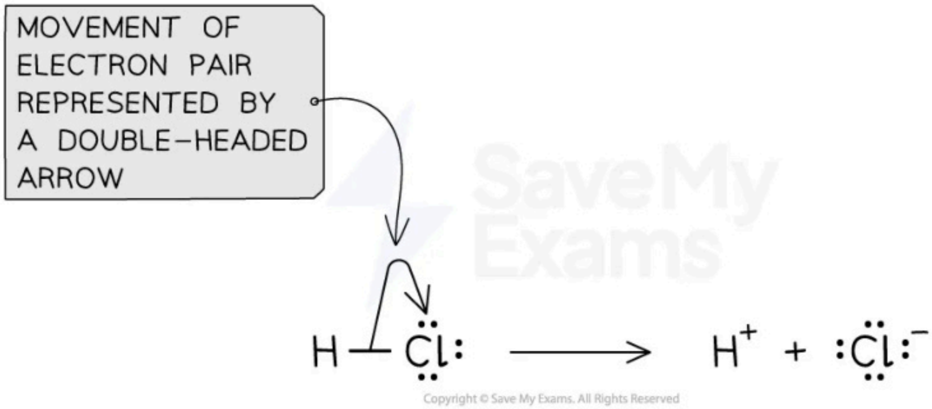
Diagram to show the process of heterolytic fission



Heterolytic fission forms a positive ion and a negative ion

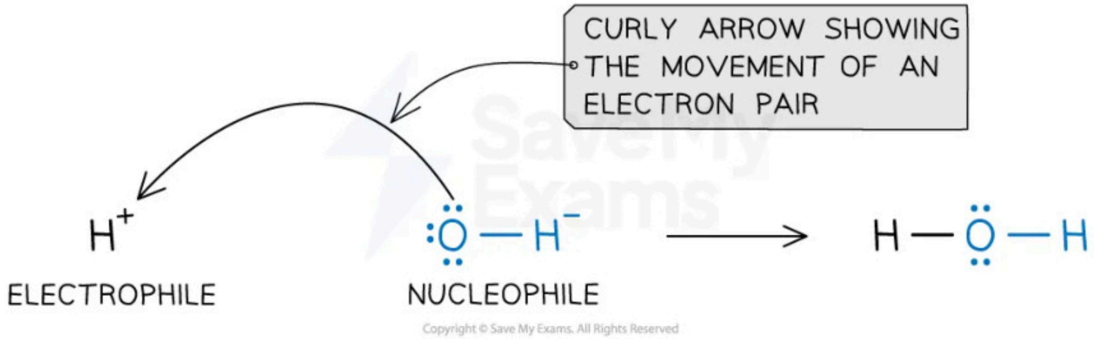
- In heterolytic fission, a double-headed arrow is used to show the movement of a **pair of electrons**
- The resulting negative ion is an electron-rich species that can **donate** a pair of electrons
  - This makes the negative ion a **nucleophile**
- The resulting positive ion is an electron-deficient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

Heterolytic fission mechanism



- 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^+

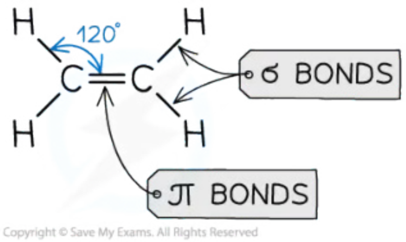
Electrophilic Addition Reactions

- **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



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

Addition reactions in alkenes

Addition of water

- When alkenes are treated with steam at **300 °C,** a pressure of **60 atmospheres** and **sulfuric acid (H_2SO_4)** or **phosphoric acid (H_3PO_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

$$CH_2CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3CH_2OH$$

ethene 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

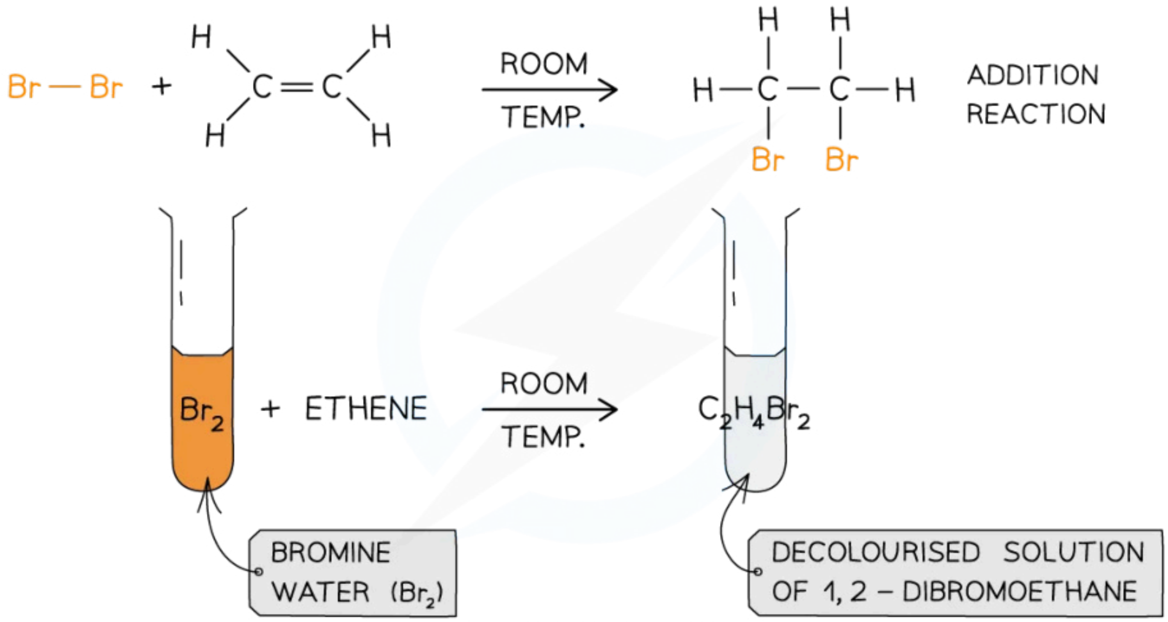
- The reaction between **alkenes** and halogens is known as **halogenation**
- It is an example of an **electrophilic addition** where an electrophile ('electron seeker') joins onto to a double bond
- The C=C double bond is broken, and a new single bond is formed from each of the two carbon atoms
- The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



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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

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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